0-315-01073-8

National Library of Canada
Canadian Theses Division
Ottawa, Canada
K1A 0N4

Bibliothèque nationale du Canada
Division des thèses canadiennes

48931

PERMISSION TO MICROFILM — AUTORISATION DE MICROFILMER

• Please print or type — Écrire en lettres moulées ou dactylographier

Full Name of Author — Nom complet de l'auteur

JEAN-FRANCOIS DUMAIS

Date of Birth — Date de naissance	Country of Birth — Lieu de naissance
1 MARCH 1951	N.B. CANADA

Permanent Address — Résidence fixe

364 DIONNE PTE AU PERE, RIMOUSKI, QUEBEC, CAN. G0K1G0

Title of Thesis — Titre de la thèse

TWO AND THREE-DIMENSIONAL INTERFACIAL DYNAMICS

University — Université

PH.D. UNIVERSITY OF ALBERTA

Degree for which thesis was presented — Grade pour lequel cette thèse fut présentée

PH.D.

Year this degree conferred — Année d'obtention de ce grade	Name of Supervisor — Nom du directeur de thèse
1980	DR. H.J. KREUZER

Permission is hereby granted to the NATIONAL LIBRARY OF CANADA to microfilm this thesis and to lend or sell copies of the film.

The author reserves other publication rights, and neither the thesis nor extensive extracts from it may be printed or otherwise reproduced without the author's written permission.

L'autorisation est, par la présente, accordée à la BIBLIOTHÈQUE NATIONALE DU CANADA de microfilmer cette thèse et de prêter ou de vendre des exemplaires du film.

L'auteur se réserve les autres droits de publication; ni la thèse ni de longs extraits de celle-ci ne doivent être imprimés ou autrement reproduits sans l'autorisation écrite de l'auteur.

Date	Signature
September 23 1980	Jean-François Dumais

NL-91 (4/77)

National Library of Canada
Collections Development Branch

Canadian Theses on
Microfiche Service

Bibliothèque nationale du Canada
Direction du développement des collections

Service des thèses canadiennes
sur microfiche

NOTICE

The quality of this microfiche is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us a poor photocopy.

Previously copyrighted materials (journal articles, published tests, etc.) are not filmed.

Reproduction in full or in part of this film is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30. Please read the authorization forms which accompany this thesis.

AVIS

La qualité de cette microfiche dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de mauvaise qualité.

Les documents qui font déjà l'objet d'un droit d'auteur (articles de revue, examens publiés, etc.) ne sont pas microfilmés.

La reproduction, même partielle, de ce microfilm est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30. Veuillez prendre connaissance des formules d'autorisation qui accompagnent cette thèse.

THIS DISSERTATION HAS BEEN MICROFILMED EXACTLY AS RECEIVED

LA THÈSE A ÉTÉ MICROFILMÉE TELLE QUE NOUS L'AVONS REÇUE

Ottawa, Canada
K1A 0N4

NL-339 (Rev. 8/80)

THE UNIVERSITY OF ALBERTA

TWO AND THREE-DIMENSIONAL INTERFACIAL DYNAMICS

by

© JEAN-FRANCOIS DUMAIS

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

OF DOCTOR OF PHILOSOPHY

IN

THEORETICAL PHYSICS

DEPARTMENT OF PHYSICS

EDMONTON, ALBERTA

FALL , 1980

THE UNIVERSITY OF ALBERTA

RELEASE FORM

NAME OF AUTHOR: Jean-François Dumais

TITLE OF THESIS: Two and Three-dimensional Interfacial Dynamics

DEGREE FOR WHICH THESIS WAS PRESENTED: Ph.D.

YEAR THIS DEGREE GRANTED: 1980

Permission is hereby granted to THE UNIVERSITY OF ALBERTA LIBRARY to reproduce single copies of this thesis and to lend or sell such copies for private, scholarly or scientific research purposes only.

The author reserves other publication rights, and neither the thesis nor extensive extracts from it may be printed or otherwise reproduced without the author's written permission.

(Signed) Jean-François Dumais

PERMANENT ADDRESS:
364 A ave Dionne,
Pointe-au-Père, P.Québec,
Canada, G0K 1G0

Dated: August 25, 1980

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled TWO AND THREE-DIMENSIONAL INTERFACIAL DYNAMICS submitted by Jean-François Dumais in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Theoretical Physics.

.....
Supervisor

.....

.....

.....

.....

.....
External examinor

Date August 25, 1980

ABSTRACT

In this work, the interface of a non-equilibrium two-phase system is viewed as a three-dimensional zone. The usual approach, wherein surface fields are postulated instead of being derived, is first critically reviewed. A theory assuming continuously varying densities in the transition zone, in conformity with modern statistical mechanical theories of the equilibrium interface, is then constructed. An exact surface balance equation is obtained, which is *formally* identical with that found in the usual approach. Complete correspondence with the latter obtains in a suitable zeroth order approximation. A hierarchy of balance equations pertaining to normal moments of order ≥ 1 is next obtained. Finally the specific cases of mass, momentum and energy are analyzed.

PREFACE

In the last two decades, many studies have been devoted to the non-equilibrium thermodynamics of fluid interfaces. The common approach consists in postulating surface densities and current densities, and then deriving balance equations relating these to the jumps of the bulk fields at the interface. No reference is made to the three-dimensional nature of the transition zone in that context.

In the equilibrium domain, there exists a well-known method, invented by Gibbs, that provides a beautifully simple and yet exact interpretation of the surface densities, in terms of the diffuse structure of the interface. The object of the present work is the extension of this method into the realm of non-equilibrium, thereby providing explicit interpretations for the quantities postulated in the common approach to the non-equilibrium interface.

In Chapter I, we give a short review of the Gibbs method in equilibrium and then a survey of pertinent theoretical work that has been done on the non-equilibrium problem.

In Chapter II, we first secure some geometric and kinematic tools and then proceed to a somewhat original and systematic development of the empirical approach to interfacial dynamics. This provides us with a background against which the more general theory that follows may be conveniently compared in all details. For lack of a better word, and not in a derogatory sense, we use

the adjective "empirical" in refering to any theory in which the three-dimensional nature of the transition zone is not explicitely recognized, and in which surface excess densities are therefore postulated instead of being derived. In presenting the empirical theory, we strive to isolate a minimal number of basic concepts and assumptions, and to derive the rest from them, appealing occasionally to well established general principles. This enables us to pinpoint those results which must be introduced on an ad hoc basis.

In Chapter III, we come to the more interesting part wherein the Gibbs scheme is extended into the realm of non-equilibrium. We first define appropriate surface normal moments that pick up the information necessary for a macroscopic two-dimensional description of the microscopic three-dimensional transition zone. We then derive an exact surface balance equation that is *formally* identical with the one used in the empirical approach, and explain why this formal identity is remarkable.Next we undertake a systematic comparison of the results obtained with those used in the empirical approach. It appears that full correspondence obtains only in a well-defined zeroth order approximation, with a wide range of validity.

In Chapter IV, we derive balance equations for higher order moments and give an application to the transversality condition derived in a (empirical) theory of Bedeaux, Albano and Mazur.

In Chapter V, we analyze the specific cases of mass, momentum and energy. While complete correspondence with the empirical approach obtains for the first two - at least in the zeroth order approximation - discrepancies appear in the case of energy, unless some residual terms, of a kind not met in the case of mass and momentum, can be neglected. These residual terms arise from the non-linearity of some energy related expressions. Interestingly, this problem is related to our identification, in Chapter II, of the treatment of energy as a weak spot, or less convincing part, in the empirical approach.

Finally a word about the labeling of equations. Equations within a given chapter are labeled according to the section in which they appear and to the order of appearance in that section. For instance, eq.(2.3) means the third equation of Section 2 of that chapter. When refering to an equation in a preceding chapter, the number of that chapter is added before the other two numbers (e.g. eq.(I.2.3)).

ACKNOWLEDGEMENTS

I would like to thank all my professors at the University of Alberta. In particular, I wish to express my very deep gratitude towards my supervisor, Dr. H.J. Kreuzer, for his advice and for the encouragement he has given me.

To the National Research Council of Canada and to the Ministère de l'Education du Québec I am indebted for financial support during the two years that I spent as a Ph.D. candidate at the University of Alberta.

Last but not least, I thank my wife Renée for her patient and skillful typing of an unwieldy manuscript.

TABLE OF CONTENTS

CHAPTER		PAGE
I	FLUID INTERFACES IN AND OUT OF EQUILIBRIUM	1
	1) Review of Gibbs equilibrium interfacial thermodynamics	1
	2) Studies of non-equilibrium interfacial systems	11
II	THEORIES POSTULATING SURFACE DENSITIES	16
	1) Geometric preliminaries	16
	2) A minimal empirical theory of the generic surface balance equation	25
	3) Mass,momentum and angular momentum balance	42
	4) Energy	54
III	THE DEVIATION APPROACH	61
	1) Towards a more general theory	61
	2) Density integrals,currents and surface normal moments	65
	3) The first surface balance equation	77
	4) The normal moment expansion of fluxes and density integrals	82
	5) The information contained in the normal moments	91
	6) Vector balance equations	97

CHAPTER		PAGE
IV	BALANCE EQUATIONS OF HIGHER NORMAL MOMENTS	99
	1) Balance equations for individual normal moments	99
	2) Balance equations for combined normal moments	106
	3) Application to the transversality condition of the BAM theory	112
V	MOMENTUM AND ENERGY	115
	1) Mass and momentum balance	115
	2) Relative velocity residuals	121
REFERENCES		128

LIST OF FIGURES

PAGE

Figure 1: The dividing surface Σ_t intersecting a fixed three-dimensional region V with boundary ∂V and outward unit normal vector $\vec{N}$. 31

Figure 2: A portion of the region $X_t(\partial V)$. 69

Figure 3: The zeroth order current excess for flat surfaces. 95

CHAPTER I

FLUID INTERFACES IN AND OUT OF EQUILIBRIUM

1) Review of Gibbs equilibrium interfacial thermodynamics

Since the object of the present work is the extension of the Gibbs approach (Gibbs [1961]) to interfacial systems into the realm of non-equilibrium, it is appropriate to start with a brief review of that approach. A thorough exposition may be found in the book by Defay et al [1966]. It will be sufficient for our present illustrative purposes to consider an equilibrium two-phase system with a flat interface. The systematic extension of the theory to equilibrium *curved* interfaces has been carried out by Buff [1956], whose contributions have been nicely reviewed by Melrose [1968,1970] The work of Buff has in turn been extended by Boruvka and Neumann [1977]. Curvature effects are also discussed by Sanfeld [1971].

For simplicity, we shall first consider a one-component system. When surface effects are neglected, all the thermodynamic information concerning the system is contained in any one of the thermodynamic potentials (U,S,H,F,G) provided these are known as functions of their natural variables. For example, knowing the Helmholtz free energy F(T,V) we get the equation of state via $p = -\frac{\partial F}{\partial V}$ and all thermal properties via $S = -\frac{\partial F}{\partial T}$. The liquid-vapor transition is also accounted for by F through flat portions of

isotherms below the critical temperature and the values of S at both ends of these flat portions give the latent heat of vaporization. Completely missing in this description however are the surface effects. But the full picture may be restored by incorporating the interfacial area among the extensive variables on which the free energy depends. Denoting by U the total energy and including for convenience the mole number N among the independent variables, the basic relations are

$$dU = TdS - p\,dV + \gamma\,dA + \mu\,dN$$

$$F = U - TS$$

$$dF = -S\,dT - p\,dV + \gamma\,dA + \mu\,dN \qquad (1.1)$$

where μ is the chemical potential and γ is by definition the surface tension. It follows that

$$\gamma = \left(\frac{\partial F}{\partial A}\right)_{T,V,N} . \qquad (1.2)$$

To visualize such a system, one may consider a container whose walls may be deformed so as to permit variation of interfacial area A at constant volume if so desired. Effects of the gravitational field other than that of providing a flat horizontal interface (away from edges) are neglected. Far away from the interface, the fluid is homogeneous. Extensive properties of bulk fluid regions are then given by volume integrals of uniform densities (neglecting external fields). Upon crossing the interface or transition zone, the values of the densities change from those appropriate to one phase to those appropriate to the other phase. Despite macroscopic appearances, these variations are not jump discontinuities

but are simply the result of very steep gradients. In simple fluids, far from the critical point, the thickness of the transition zone is of the order of a few molecular diameters (Lekner and Henderson [1978], Goodisman [1979]). The determination of the density profile inside this region is one of the main problems considered in the equilibrium statistical mechanics of fluid interfaces developed especially in the last two decades (Navascués [1979], Croxton [1978]). Experimental investigations based on light ellipticity have been reported (Beaglehole [1979]), but computer experiments are the more usual testing ground.

The diffuse nature of the transition zone implies that the partitioning of fluid attributes into contributions from both phases and from the interface is not unique. Now, in macroscopic physics, one is not interested in the detailed structure of the interface, and Gibbs has introduced a beautifully simple and yet rigorous way of keeping track of the interfacial contributions, while discarding irrelevant microscopic information. It consists first in introducing a dividing surface (simply an abstract mathematical surface) located somewhere in the transition zone and in extrapolating the constant values of the bulk densities in either phase up to this surface Σ. Inasmuch as the transition zone, despite its extreme thinness, is diffuse, the computation, with such extrapolated densities, of the total amount of an attribute in a region V encompassing a patch from the interface will usually be in error. The second aspect of the Gibbs scheme consists

in correcting these errors by compensating surface excess quantities, which are the surface integrals of superficial densities defined on the dividing surface Σ. This method is very attractive and widely used because it is in tune with macroscopic intuition and yet extremely general and exact. This last feature is not always appreciated as the scheme is now and then refered to as the "Gibbs approximation" in the literature.

The gist of the approach can be clearly illustrated through Gibbs' definition of adsorption. Consider a two-phase fluid mixture with bulk mole number *densities* $n_1^\alpha,\ldots,n_n^\alpha$, where the superscript $\alpha = +,-$ identifies the phase. Le us denote by $N_i^*(V)$ the exact mole number of species i contained in a cubical region V with two faces parallel to Σ. The dividing surface splits this region V into two subsets V^+ and V^- and $N_i^*(V)$ is written as

$$N_i^*(V) = \int_{V^+} n_i^+ \, dV + \int_{V^-} n_i^- \, dV + \int_{\Sigma(V)} \Gamma_i \, dA \qquad (1.3)$$

$$= n_i^+ V^+ + n_i^- V^- + \Gamma_i A$$

where $\Sigma(V) \equiv \Sigma \cap V$ is that part of Σ contained in V and Γ_i is by definition the *adsorption* of component i. It is an intensive surface variable. Denoting by ζ the coordinate on an axis perpendicular to Σ ($\zeta = 0$ on Σ) and by n_i^* the exact mole number densities, which vary continuously across the transition zone, it follows immediately that

$$\Gamma_i = \int_{-\infty}^{0} (n_i^*(\zeta) - n_i^-) \, d\zeta + \int_{0}^{\infty} (n_i^*(\zeta) - n_i^+) \, d\zeta \qquad (1.4)$$

The diffuse nature of the transition zone confers a degree of arbitrariness to the choice of the dividing surface, and the values of the surface densities usually depend on this choice. This dependence on the location of Σ is easily understood in the case of the adsorptions defined above. Let us assume for example that $n_i^+ < n_i^-$, and that $n_i^*(\zeta)$ is monotonous across the transition zone. If the dividing surface is located at a value of ζ where n_i^* has reached the value n_i^+, it is clear that Γ_i will be negative because the sum of the integrals of the bulk densities then overestimates $N_i^*(V)$. On the contrary, putting Σ at a value of ζ where n_i^* has reached the value n_i^- leads to an underestimation of the mole number and thus to a positive value of Γ_i. This case provides a dramatic illustration of the possible sensitiveness of surface density values on the location of the dividing surface: by moving Σ within the extremely narrow margin delimited by the transition zone, the adsorption Γ_i can even be made to change sign ! There are however noteworthy exceptions to this type of behavior. Let a^* denote the exact density of some attribute, with corresponding bulk densities a^+ and a^-. It is clear that the associated surface excess a^s will be independent of the dividing surface position if $a^+ = a^-$. One case in point is the surface tension of a flat interface (Green [1969]). Another example of almost complete invariance is that of a dilute solution of a strong surfactant (Lucassen-Reynders [1976], p.282). This invariance explains why surface chemists can refer loosely to the adsorption as "number of molecules per unit area of adsorbed film" without running into inconsistencies.

Even in cases where the surface densities depend sensibly on the choice of the dividing surface, the theory can be fully developed leaving that choice open. The choice of a particular dividing surface becomes then largely a matter of convenience and varies with the context. Usually specific choices are formulated in terms of adsorptions, for instance by requiring the adsorption of a certain component to vanish (Defay et al [1966], p.27).

To further illustrate the working of the equilibrium theory we shall briefly consider the surface Helmholtz free energy in a one-component system. Once the values of T,V,A,N are given, assuming that some convention (which need not be specified) has been made on the choice of the dividing surface Σ, the total free energy is written as

$$F(T,V,A,N) = F^{+}(T,V^{+},N^{+}) + F^{-}(T,V^{-},N^{-}) + F^{S}(T,V,A,N) \quad (1.5)$$

where the values of V^{+},N^{+},V^{-},N^{-} depend on the choice of Σ. The free energies F^{+},F^{-} refer to the two bulk phases and F^{S} is the surface excess. The pressure in the system is known and so are the mole number densities n^{+} and n^{-} in the bulk regions. Now let us, at fixed interfacial area, change the mole numbers in the bulk phases by adding isothermally amounts ΔN^{+} and ΔN^{-} and changing the volumes so as to accomodate this new material without changing any of the intensive variables (whose values, according to the phase rule, are all determined by T along the liquid-vapor coexistence line). This may be achieved by taking $\Delta V^{+} = \frac{1}{n^{+}}\Delta N^{+}$ and $\Delta V^{-} = \frac{1}{n^{-}}\Delta V^{-}$. The new overall volume and mole numbers are denoted by V' and N'. Clearly the varia-

tion $F(T,V',A,N') - F(T,V,A,N)$ will be fully accounted for by the variations of the first two terms on the right-hand side of (1.5). We have

$$\begin{pmatrix} V' \\ N' \end{pmatrix} = \begin{pmatrix} V \\ N \end{pmatrix} + \begin{pmatrix} 1/n^+ & 1/n^- \\ 1 & 1 \end{pmatrix} \begin{pmatrix} \Delta N^+ \\ \Delta N^- \end{pmatrix}$$

where, since $n^+ \neq n^-$, the above 2×2 matrix is invertible. It follows that V and N can be varied independently without affecting the value of the last term in eq.(1.5). Whence F^S is actually independent of V and N and depends only on A and T. Furthermore, it follows by homogeneity that at fixed T, F^S is proportional to A, that is $F^S(T,A) = A f^S(T)$. We may thus finally write

$$F(T,V,N,A) = F^+(T,V^+,N^+) + F^-(T,V^-,N^-) + A f^S(T) . \qquad (1.6)$$

We emphasize that the explicit form of this function $f^S(T)$ depends on the choice of the dividing surface. As we shall see below, its physical meaning is most transparent when the dividing surface is chosen so that the adsorption, which in the present case is given by

$$\Gamma = \frac{N^S}{A} \equiv \frac{N - N^+ - N^-}{A} , \qquad (1.7)$$

vanishes. We note incidentally that the left-hand side of eq.(1.5) makes no reference whatsoever to a dividing surface, which implies that the surface tension (see eq.(1.2)) is independent of its location. In principle we could work with this thermodynamic potential F only. But the decomposition effected in eq.(1.6) is more effective in assessing surface behavior. The *functions* F^+ and F^- are also independent of the choice of Σ, but V^+, V^-, N^+ and N^- are not,

which is why the values of the first two terms on the right-hand side of eq.(1.6) do depend on the location of Σ.

A number of thermodynamic relations may now be easily obtained. We first decompose the energy and the entropy in the same manner as the free energy:

$$\begin{aligned} U(T,V,A,N) &= U^+(T,V^+,N^+) + U^-(T,V^-,N^-) + U^S(T,A) \\ S(T,V,A,N) &= S^+(T,V^+,N^+) + S^-(T,V^-,N^-) + S^S(T,A) \end{aligned} \tag{1.8}$$

so that

$$F^S = U^S - TS^S . \tag{1.9}$$

Differentiating eq.(1.6) we get

$$\begin{aligned} -S\,dT - p\,dV + \gamma\,dA + \mu\,dN = &-S^+dT - p\,dV^+ + \mu\,dN^+ \\ &- S^-dT - p\,dV^- + \mu\,dN^- + dF^S . \end{aligned}$$

When combined with eqs.(1.8) and (1.9) this gives

$$dF^S = -S^S dT + \gamma\,dA + \mu\,dN^S \tag{1.10}$$

$$dU^S = T\,dS^S + \gamma\,dA + \mu\,dN^S . \tag{1.11}$$

One must be careful not to misinterpret these relations: T,A and N^S are *not* independent variables.

Integrating eq.(1.11) at constant temperature yields

$$U^S = TS^S + \gamma A + \mu N^S \tag{1.12}$$

from which, using eq.(1.9),

$$F^S = \gamma A + \mu N^S = (\gamma + \mu\Gamma)A . \tag{1.13}$$

Upon differentiating the last relation and comparing with eq.(1.10), we obtain a surface analogue of the Gibbs-Duhem relation, known as the Gibbs equation:

$$d\gamma = -s^S dT - \Gamma\,d\mu . \tag{1.14}$$

When the $\Gamma = 0$ convention is adopted for the choice of the dividing surface, eq.(1.13) reduces to

$$f^S = \gamma \ . \tag{1.15}$$

This is in agreement with the fact that γ depends only on temperature in a one component system. We note that the identification between γ and surface free energy per unit area obtains only when the $\Gamma = 0$ convention is adopted. Discussions of the temperature dependence of γ may be found in Defay et al [1966], Gugenheim [1965], Buff [1968] and Bikerman [1970]. Equation (1.14) also provides an interesting relation between γ and the surface entropy per unit area in the $\Gamma = 0$ convention:

$$s^S = - \frac{d\gamma}{dT} \ . \tag{1.16}$$

Naturally S^S is related to thermal effects. Let us consider a change of the area A at fixed T,V,N. In principle, a variation of A at fixed T and N implies a certain redistribution of matter from bulk to interface, and may thus entail some variation of V. But, unless a very large amount of area is created, such a change will obviously be so small as to be completely negligible. The heat absorbed by the system in the course of such a reversible isothermal expansion is given by

$$\bar{d}Q = T \, dS_N$$

where S_N denotes the total entropy at fixed N. We thus have

$$\left(\frac{\bar{d}Q}{dA} \right)_T = T \left(\frac{\partial S}{\partial A} \right)_{T,V,N} \ .$$

Since $S = -\left(\frac{\partial F}{\partial T}\right)_{V,A,N}$, it follows from eq.(1.2) that

$$\frac{\partial S}{\partial A} = -\frac{\partial^2 F}{\partial A \partial T} = -\frac{\partial^2 F}{\partial T \partial A} = -\frac{d\gamma}{dT} ,$$

so that

$$\left(\frac{đQ}{dA}\right)_T = -T\frac{d\gamma}{dT} . \qquad (1.17)$$

Together with eq.(1.16) this implies that, *with the* $\Gamma = 0$ *convention*,

$$\left(\frac{đQ}{dA}\right)_T = Ts^S . \qquad (1.18)$$

In the general case, this is replaced by

$$\left(\frac{đQ}{dA}\right)_T = T\left(s^S + \Gamma\frac{d\mu}{dT}\right) . \qquad (1.19)$$

All the above relations in which the $\Gamma = 0$ convention is not adopted may be generalized in straightforward fashion to multicomponent systems simply by replacing terms involving Γ and μ by sums of terms involving the individual adsorptions Γ_i and chemical potentials μ_i (Kirkwood and Oppenheim [1961]).

The equilibrium statistical mechanics of the fluid interface has undergone significant developments in the last two decades (Navascues [1979], Croxton [1978]). It makes extensive use of reduced distribution functions and is based on the idea of continuously varying exact densities in the transition zone, whose meaning is based on probability. The theory of Chapter III rests in part on the assumption that such meaningful densities also exist out of equilibrium.

2) Studies of non-equilibrium interfacial systems

In this section, we present a brief survey of studies devoted to the non-equilibrium fluid interface in an attempt to put the present work into proper perspective. In view of the overwhelming abundance of related literature, we shall restrict ourselves to a narrow path that will lead us to the more recent studies to which the present work is connected. For reviews, the reader is refered to Levich and Krylov [1969], Lucassen-Reynders and Lucassen [1977], Defay,Prigogine and Sanfeld [1977],Ostrach [1979]. An extensive bibliography covering older work, particularly in connection with free thin liquid films, may be found in Mysels [1959].

The most well-known phenomena in relation with interfacial motion are probably the Gibbs and Marangoni effects (Kitchener [1964]). The Gibbs effect is in reality a static type of elasticity operative in thin liquid films (Krotov and Rusanov [1972]). When a thin film of a surfactant solution is stretched, the interfacial area on both of its faces increases. As a result, additional surface-active solute migrates from the internal solution which is thus depleted with respect to the solute. In the new equilibrium that is established, it follows that the surface tension is higher. Compression of the film naturally produces the opposite effect. It is obvious that this effect must depend on the film thickness. A thermodynamic theory has been given by van den Tempel,Lucassen and Lucassen-Reynders [1965].

The Marangoni effect (Scriven and Sternling [1960]) is related to the Gibbs effect but does not hinge upon the thinness of

bulk substrate. When the interface of a solution of a surface-active agent is rapidly expanded, there results an impoverishment in solute near the interface, which is accompanied by an increase in surface tension. The reestablishment of equilibrium is delayed by the diffusion of solute in the bulk. This explains why a transient higher surface tension may exist without the requirement of a thin bulk phase, as opposed to the Gibbs effect. The best known early theoretical investigation in that field is that of Ward and Tordai [1946]. Further significant developments were made by Baret [1968] whose work contained a mistake later corrected by Petrov and Miller [1977]. A modern review of dynamic surface tension has been given by Defay and Petré [1971].

Another important concept in relation with the fluid interface is the so-called surface viscosity. This concept was introduced apparently for the first time by Boussinesq [1913] and later formalized by Ericksen [1952], Oldroyd [1955] and Scriven [1960]. The theory accomodates shear as well as dilatational viscosity (Slattery [1978]). Non newtonian behavior has also been considered (Addison and Schechter [1978]). Reviews have been given by Joly [1964] and Goodrich [1973]. Another phenomenon that has been studied is surface diffusion (Brenner and Leat [1978] and refs therein).

In 1959, Sternling and Scriven made the first attack on the problem of interfacial instability and turbulence. Interest in this problem has been recently revived (Hennenberg et al [1980] and refs. therein).

Certainly a landmark in the subject of interfacial dynamics was the paper by Scriven [1960]. It was followed by a series of investigations by various authors leading to recent systematic applications of non-equilibrium thermodynamics . His work made no explicit reference to the Gibbs approach and was in the spirit of the empirical approach discussed in Chapter II of this thesis. In a first step, Scriven took an intrinsic view of the interface without reference to the adjacent bulk phases and wrote down equations of motion within this two-dimensional world. In a second step, he considered the connection with the bulk phases. A pedagogical and detailed exposition of the scheme invented by Scriven has been given by Aris [1962].

Scriven derivations however entailed some conceptual difficulties which were pointed out and corrected in a generalization taking proper account of mass transfer across the interface by Slattery [1964].

Next came a paper by Ghez [1965] containing two innovations. First, the generic surface balance equation (at the empirical level) was derived; secondly, it was the first time (to our knowledge) that the standard methods of linear irreversible thermodynamics were brought to bear on the problem (though it was only later that they were fully exploited). Building upon the work of Ghez, Georgescu [1969] considered momentum balance at an interface with internal angular momentum. Ghez also made specific applications of his theory (Ghez [1970]).

Waldam [1967] also applied the methods of irreversible thermodynamics, though without considering surface energy, to the boundary conditions at the interface of two immiscible fluids. His work was generalized in a paper by Bedeaux, Albano and Mazur [1976], who included surface energy thus bringing in surface tension. These authors set up a formalism (hereafter refered to as the BAM theory) that has since then been used in several other investigations. Their work has been extended first by Kovak [1977] and by Vodák [1978 b] to a multicomponent system with what they call singular mass densities at the interface. The entropy production at the interface in such systems has a rather involved structure and there results a rich supply of phenomenological coefficients. The theory was further generalized by Wolf and Albano [1979] to accommodate electromagnetic fields.

We should also mention another work of more limited scope by Popielawski [1970] and a careful treatment of diffusion related matters by Kehlen and Baranowski [1977].

Other approaches, in the spirit of rational thermodynamics, have also been made (Moeckel [1975], Murdoch [1976]).

A common feature of the above theories is that, in their context, surface densities are *postulated* instead of being derived and that they at best only implicitely acknowledge the three-dimensional nature of the interface. Interfacial balance equations were investigated by Slattery [1967] from a more fundamental point of view according to which the transition zone is three-dimensional.

This is in agreement with modern equilibrium statistical mechanics theories of surface tension and related matters (Navascues [1979]). Slattery presented his work as a generalization of the work of Buff [1956] on equilibrium two-phase systems (further developments in this equilibrium theory were made by Boruvka and Neumann [1977]). In the present study, specifically from Chapter III onward, we start from the same basic premises that were neatly formulated in this paper of Slattery and carry the theory considerably further so that all the aspects of the empirical approach may be interpreted in terms of appropriate surface normal moments. Some of our results have been reported in a paper which will appear in Physica A. The same problem has been approached differently by Ronis, Bedeaux and Oppenheim [1978] and by Albano, Bedeaux and Vlieger [1979]. An approximate derivation of the surface balance equation was also given by Deemer and Slattery [1978].

In the next chapter, we shall look at interfacial balance equations from the empirical point of view, that is without refering to the diffuse nature of the transition zone. This will provide us with a background against which the subsequent theory may be compared.

CHAPTER II

THEORIES POSTULATING SURFACE DENSITIES

1) Geometric preliminaries

In this section we set up the notations used throughout this work, discuss some key geometrical concepts and derive some kinematic results needed in the subsequent discussion. The first part is concerned with the calculus and geometry of surfaces and the second part is concerned with their motions. We shall view a surface as a two-dimensional submanifold of the three-dimensional space E_3, with or without boundary. Surfaces with self-intersections are thus excluded.

The tangent plane to a surface Σ at a point $\vec{p}$ of Σ is a two-dimensional vector space denoted by $T_{\vec{p}}(\Sigma)$. *To indicate that a vector is tangent to Σ, we will put a bar over it.* Any vector $\vec{X} \in E_3$ may be decomposed into its normal and tangential components at $\vec{p} \in \Sigma$:

$$\vec{X} = P_{\vec{p}}(\vec{X}) + \vec{X}\cdot\vec{n}\,\vec{n} \qquad (\vec{n}\cdot P_{\vec{p}}(\vec{X}) = 0) \ , \tag{1.1}$$

where $P_{\vec{p}}$ is the projector on $T_{\vec{p}}(\Sigma)$ and $\vec{n}$ is the unit normal vector to Σ at $\vec{p}$. The directional derivative at $\vec{p}$, with respect to $\bar{u} \in T_{\vec{p}}(\Sigma)$, of a function f (resp. a vector field $\vec{X}$) defined on Σ is defined by

$$D_{\bar{u}} f(\vec{p}) = \frac{d}{d\xi} f(\vec{c})(0) \qquad (\text{resp. } D_{\bar{u}} \vec{X}(\vec{p}) = \frac{d}{d\xi} \vec{X}_{\vec{c}}(0) \ ) \qquad (1.2)$$

where $\xi \to \vec{c}(\xi)$ is any curve on Σ such that $\vec{c}(0) = \vec{p}$ and $\frac{d\vec{c}}{d\xi}(0) = \bar{u}$.

If $\vec{R}(\xi^1, \xi^2)$ is a parametrization of Σ around $\vec{p} \in \Sigma$, and $\bar{u} = u^1 \frac{\partial \vec{R}}{\partial \xi^1} + u^2 \frac{\partial \vec{R}}{\partial \xi^2}$, then

$$D_{\bar{u}} f(\vec{p}) = u^1 \frac{\partial}{\partial \xi^1} (f \circ \vec{R})(\vec{p}) + u^2 \frac{\partial}{\partial \xi^2} (f \circ \vec{R})(\vec{p})$$

and likewise

$$D_{\bar{u}} \vec{X}(\vec{p}) = u^1 \frac{\partial}{\partial \xi^1} (\vec{X} \circ \vec{R})(\vec{p}) + u^2 \frac{\partial}{\partial \xi^2} (\vec{X} \circ \vec{R})(\vec{p})$$

where the symbol " $\circ$ " stands for the composition of functions. Note that $\bar{u}$ need not be a unit vector and that both $D_{\bar{u}} f(\vec{p})$ and $D_{\bar{u}} \vec{X}(\vec{p})$ are linear in $\bar{u}$, at fixed $\vec{p}$. Thus the vector $\mathrm{Grad} f(\vec{p}) \in T_{\vec{p}}(\Sigma)$ is defined by

$$D_{\bar{u}} f(\vec{p}) = \bar{u} \cdot \mathrm{Grad} f(\vec{p}) \quad \text{for every } \bar{u} \in T_{\vec{p}}(\Sigma). \qquad (1.3)$$

The *covariant derivative at* $\vec{p}$, *with respect to* $\bar{u} \in T_{\vec{p}}(\Sigma)$, of a *tangent* vector field $\bar{X}$ defined on Σ, $\bar{\nabla}_{\bar{u}} \bar{X}(\vec{p})$, is defined as the projection on the tangent plane of its directional derivative:

$$\bar{\nabla}_{\bar{u}} \bar{X}(\vec{p}) = P_{\vec{p}}[D_{\bar{u}} \bar{X}(\vec{p})] \quad . \qquad (1.4)$$

At fixed $\vec{p}$, the map $\bar{u} \to \bar{\nabla}_{\bar{u}} \bar{X}(\vec{p})$ is clearly a linear operator on $T_{\vec{p}}(\Sigma)$; it is denoted by $(\bar{\nabla} \bar{X})_{\vec{p}}$ and called the *covariant derivative of* $\bar{X}$ *at* $\vec{p}$. Hence by definition,

$$[\bar{\nabla} \bar{X}]_{\vec{p}}(\bar{u}) = \bar{\nabla}_{\bar{u}} \bar{X}(\vec{p}) \quad \text{for every } \bar{u} \in T_{\vec{p}}(\Sigma). \qquad (1.5)$$

Given a linear operator $A : T_{\vec{p}}(\Sigma) \to T_{\vec{p}}(\Sigma)$, its trace will be denoted by $\overline{\mathrm{Tr}}(A)$. (The bar emphasizes that we are dealing with a two-dimensional vector space.) Given a tangent vector field $\bar{X}$ on Σ, the diver-

gence of $\bar{X}$ at $\vec{p} \in \Sigma$ is defined as the trace of its covariant derivative at $\vec{p}$:

$$\mathrm{Div}\,\bar{X}(\vec{p}) = \overline{\mathrm{Tr}}[\bar{\nabla}\bar{X}]_{\vec{p}} . \tag{1.6}$$

Let A be a field of linear operators on Σ, which to each $\vec{p}$ associates a linear operator $A_{\vec{p}}$ that maps $T_{\vec{p}}(\Sigma)$ into itself. The covariant derivative of A at $\vec{p}$, with respect to $\bar{u} \in T_{\vec{p}}(\Sigma)$, is defined by

$$(\bar{\nabla}_{\bar{u}}A)_{\vec{p}} = P_{\vec{p}}(D_{\bar{u}}AP)_{\vec{p}} \quad \text{(restricted to } T_{\vec{p}}(\Sigma)) . \tag{1.7}$$

At fixed $\vec{p}$ *and* $\bar{u}$ this is, just like $A_{\vec{p}}$, a linear operator on $T_{\vec{p}}(\Sigma)$ and it is easily seen that $(\bar{\nabla}_{\bar{u}}A)^*_{\vec{p}} = (\bar{\nabla}_{\bar{u}}A^*)_{\vec{p}}$, (where A^* denotes the adjoint of A) and that $\bar{\nabla}_{\bar{u}}[A(\bar{X})] = (\bar{\nabla}_{\bar{u}}A)(\bar{X}) + A(\bar{\nabla}_{\bar{u}}\bar{X})$, where $\bar{X}$ is any vector field on Σ. Finally the divergence of A at $\vec{p}$ is a vector $\mathrm{Div}A(\vec{p}) \in T_{\vec{p}}(\Sigma)$ defined by

$$\mathrm{Div}A(\vec{p}) = [\bar{\nabla}_{\bar{u}_1}A]^*_{\vec{p}}(\bar{u}_1) + [\bar{\nabla}_{\bar{u}_2}A]^*_{\vec{p}}(\bar{u}_2) , \tag{1.8}$$

where $(\bar{u}_1,\bar{u}_2)$ is any orthonormal basis of $T_{\vec{p}}(\Sigma)$. If $\bar{X}$ is a tangent vector field on Σ, the following identity holds:

$$\mathrm{Div}[A(\bar{X})] = \bar{X}\cdot\mathrm{Div}A + \overline{\mathrm{Tr}}(A\,\bar{\nabla}\bar{X}) \tag{1.9}$$

where $\bar{\nabla}\bar{X}$ is the covariant derivative of $\bar{X}$ (see eq.(1.5)) .

On each tangent plane $T_{\vec{p}}(\Sigma)$ of a surface Σ is defined a linear operator $S_{\vec{p}} : T_{\vec{p}}(\Sigma) \to T_{\vec{p}}(\Sigma)$, called the *shape operator of* Σ *at* $\vec{p}$ (O'Neill [1970]), which tells how the unit normal $\vec{n}$ to Σ changes in the neighborhood of $\vec{p}$. Specifically, if $\bar{u} \in T_{\vec{p}}(\Sigma)$, we have

$$\vec{n}(\vec{p}) \cdot D_{\bar{u}}\vec{n}(\vec{p}) = \tfrac{1}{2} D_{\bar{u}}\,\vec{n}\cdot\vec{n}(\vec{p}) = 0$$

since $\vec{n}\cdot\vec{n}$ is constant (=1). It follows that $D_{\bar{u}}\vec{n}(\vec{p}) \in T_{\vec{p}}(\Sigma)$. The shape operator at $\vec{p}$, $S_{\vec{p}}$, is the linear operator on $T_{\vec{p}}(\Sigma)$ defined by

$$S_{\vec{p}}(\bar{u}) = - D_{\bar{u}}\vec{n}(\vec{p}) \qquad \text{for every } \bar{u} \in T_{\vec{p}}(\Sigma). \tag{1.10}$$

(The operator $L_{\vec{p}} = -S_{\vec{p}}$ is usually called the Weingarten map, whereas the twice covariant tensor associated to $S_{\vec{p}}$ is called the second fundamental form.) It may be shown (Hicks [1965]) that the shape operator is self-adjoint, that is

$$\bar{u}\cdot S_{\vec{p}}(\bar{v}) = S_{\vec{p}}(\bar{u})\cdot\bar{v} \quad \text{for every } \bar{u},\bar{v} \in T_{\vec{p}}(\Sigma) \ . \tag{1.11}$$

Given a unit vector $\bar{u} \in T_{\vec{p}}(\Sigma)$, the plane through $\vec{p}$, spanned by $\vec{n}(\vec{p})$ and $\bar{u}$, cuts Σ along a curve $\Gamma_{\bar{u}}$ called a normal section at $\vec{p}$. The normal curvature of Σ at $\vec{p}$ in the $\bar{u}$ direction, $\kappa_{\vec{p}}(\bar{u})$, is by definition equal to the curvature of the normal section $\Gamma_{\bar{u}}$ at $\vec{p}$, counted as positive when $\Gamma_{\bar{u}}$ bends toward $\vec{n}(\vec{p})$. It may be shown that (O'Neill [1970])

$$\kappa_{\vec{p}}(\bar{u}) = \bar{u}\cdot S_{\vec{p}}(\bar{u}) \ . \tag{1.12}$$

Since $S_{\vec{p}}$ is self-adjoint, it has two real eigenvalues k_1, k_2, called the principal curvatures of Σ at $\vec{p}$. From eq.(1.12) these are the extreme values of the normal curvature at $\vec{p}$. The mean and Gaussian curvatures of Σ are defined respectively by

$$H = \tfrac{1}{2}(k_1+k_2) = \tfrac{1}{2}\overline{\mathrm{Tr}}\,S \quad \text{and} \quad K = k_1k_2 = \det S \ . \tag{1.13}$$

The sign of $K(\vec{p})$ tells much about the shape of Σ in the neighborhood of $\vec{p}$ (O'Neill [1970],p.204).

If $\bar{u} \in T_{\vec{p}}(\Sigma)$ and $\bar{X}$ is a tangent vector field on Σ, $\vec{n}\cdot D_{\bar{u}}\bar{X} = -\bar{X}\cdot D_{\bar{u}}\vec{n} = \bar{X}\cdot S(\bar{u})$, a result which combined with eq.(1.4) implies the Gauss equation

$$D_{\bar{u}}\bar{X} = \bar{\nabla}_{\bar{u}}\bar{X} + \bar{u}\cdot S(\bar{X})\,\vec{n} \ . \tag{1.14}$$

An immediate consequence of this equation is that if $\vec{A}$ is a *constant* vector and $\bar{A}$ is the tangent vector field defined on Σ by

$\overline{A}_{\vec{p}} = P_{\vec{p}}(\vec{A})$, then the covariant derivative of $\overline{A}$ (defined by eq.(1.5)) is given by

$$\overline{\nabla A} = \vec{A}\cdot\vec{n}\, S \quad . \tag{1.15}$$

Finally we consider a moving surface. This will be viewed as a one-parameter family of surfaces Σ_t, one for each time t, such that there exists a reference configuration Σ^0 and a differentiable function $\vec{R}(t,\vec{p})$, $\vec{p} \in \Sigma^0$,with the property that the map $\vec{R}_t:\Sigma^0 \to \Sigma_t$: $\vec{p} \to \vec{R}_t(\vec{p}) = \vec{R}(t,\vec{p})$ is a diffeomorphism. The reference configuration Σ^0 need not coincide with any of the surfaces of the family. Moreover given the one-parameter family Σ_t and the reference configuration Σ^0, the parametrization $\vec{R}(t,\vec{p})$ is not unique. We will return to this point shortly. The normal speed $v^\perp$ of the moving surface at $\vec{p} = \vec{P}(t) \in \Sigma_t$ is defined by

$$\frac{d\vec{P}}{dt}(t) = v^\perp \vec{n}(\vec{p}) \tag{1.16}$$

where $\vec{P}$ is the trajectory defined by $\vec{P}(t) = \vec{p}$, $\vec{P}(t') \in \Sigma_t$, and $\vec{n} \times \frac{d\vec{P}}{dt}(t') = \vec{0}$ for every t'. If a function f is defined on the moving surface (that is a function f_t is given on each Σ_t) the normal time derivative of f, $\frac{d^\perp f}{dt}$, is defined by

$$\frac{d^\perp f}{dt} = \frac{d}{dt} f(\vec{P}) \tag{1.17}$$

where the trajectory $\vec{P}$ is as above. Given any trajectory $\vec{q}(t)$ such that $\vec{q}(t) \in \Sigma_t$ for each t, it may be shown (Treusdell [1960]) that

$$\vec{n}\cdot\dot{\vec{q}} = v^\perp \tag{1.18}$$

and that

$$\frac{d}{dt} f(\vec{q}) = \frac{d^\perp f}{dt} + \dot{\vec{q}}_{/\!/}\cdot \mathrm{Grad}\, f \qquad (\dot{\vec{q}}_{/\!/} \equiv P(\dot{\vec{q}})) \quad . \tag{1.19}$$

If a tangent vector field $\bar{X}$ is defined on the moving surface and $\bar{X}_{\vec{q}}$ is the vector-valued function of time $\bar{X}_{\vec{q}}(t) = (\bar{X})_{\vec{q}(t)}$, and if $(\vec{e}_1,\vec{e}_2,\vec{e}_3)$ is a fixed orthonormal frame, then

$$\dot{\vec{q}}_{/\!/}\cdot\mathrm{Grad}\,(\vec{e}_i\cdot\bar{X}) = \vec{e}_i\cdot\bar{\nabla}_{\dot{\vec{q}}_{/\!/}}\bar{X} + \bar{X}\cdot\bar{\nabla}_{\dot{\vec{q}}_{/\!/}}\bar{e}_i = \vec{e}_i\cdot[\bar{\nabla}_{\dot{\vec{q}}_{/\!/}}\bar{X} + \bar{X}\cdot S(\dot{\vec{q}}_{/\!/})\vec{n}]$$

where use has been made of eq.(1.15). Together with eq.(1.19) this implies

$$\frac{d\,\bar{X}_{\vec{q}}}{dt} = \frac{d^{\perp}\bar{X}}{dt} + \bar{\nabla}_{\dot{\vec{q}}_{/\!/}}\bar{X} + \dot{\vec{q}}_{/\!/}\cdot S(\bar{X})\vec{n} \quad . \tag{1.20}$$

We shall finally derive expressions for the rate of change of the unit normal and local area of a moving surface in terms of its normal velocity field. Given two surfaces Σ and Σ', and a smooth map $\vec{M} : \Sigma \to \Sigma'$ between them, the differential of $\vec{M}$ at $\vec{p} \in \Sigma$, denoted by $\vec{M}_{*\vec{p}}$, is the linear map between $T_{\vec{p}}(\Sigma)$ and $T_{\vec{p}'}(\Sigma')$ $(\vec{p}' = \vec{M}(\vec{p}))$ defined by

$$\vec{M}_{*\vec{p}}(\bar{u}) = D_{\bar{u}}\vec{M}(\vec{p}) \quad \text{for every } \bar{u} \in T_{\vec{p}}(\Sigma) \; . \tag{1.21}$$

Given $\vec{p} \in \Sigma$, the jacobian of $\vec{M}$ at $\vec{p}$, $J(\vec{p})$, is defined by

$$J(\vec{p}) = \vec{n}'\cdot(\vec{M}_{*\vec{p}}(\bar{u}_1)\times M_{*\vec{p}}(\bar{u}_2)) \quad ,$$

where $(\bar{u}_1,\bar{u}_2)$ is any orthonormal basis of $T_{\vec{p}}(\Sigma)$ such that $\vec{n}\cdot(\bar{u}_1\times\bar{u}_2) = 1$ and $\vec{n}'$ is the unit normal to Σ' at $\vec{p}' = \vec{M}(\vec{p})$. The intuitive meaning of the jacobian is revealed by the change of variable formula :

$$\int_{\Sigma'} f\, dA' = \int_{\Sigma} f\circ\vec{M}\,|J|\, dA \tag{1.22}$$

where dA and dA' are the area elements on Σ and Σ' and f is any integrable function on Σ'.

Coming back to a moving surface Σ_t, we assume that its

motion may be described with the help of a reference configuration $\Sigma^0 = \Sigma_{t_0}$ and of a smooth function $\vec{R}(t,\vec{p})$, $\vec{p} \in \Sigma^0$, such that, at fixed t, the map $\vec{R}_t : \Sigma^0 \to \Sigma_t : \vec{p} \to \vec{R}_t(\vec{p}) = \vec{R}(t,\vec{p})$ is a diffeomorphism between Σ^0 and Σ_t. This brings up a subtle point with incidence on the theory that follows. If the moving surface Σ_t were a model of say a membrane, there would be a natural choice of the function $\vec{R}(t,\vec{p})$ as a "material" parametrization, in the sense that $\vec{R}(t,\vec{p})$ would be the position at time t of the membrane "particle" which occupied the position $\vec{p}$ in the reference configuration $\Sigma^0 = \Sigma_{t_0}$ at time t_0. But when Σ_t is of an abstract nature, with no "material" existence, as is the case with the dividing surfaces considered below, there is no such natural choice. In fact it is clear that given a moving surface Σ_t and a particular parametrization $\vec{R}(t,\vec{p})$, we can find infinitely many other different parametrizations simply by superposing internal "motions" within the moving surface. However, given the one-parameter family Σ_t, all these different parametrizations have in common the normal component of their velocity field for, according to eq.(1.18), we have

$$\vec{n} \cdot \frac{\partial \vec{R}}{\partial t} = v^{\perp}$$

where $v^{\perp}$ is defined by eq.(1.16). Given some reference configuration Σ_{t_0}, this leads us to define the normal parametrization $\vec{R}^{\perp}(t,\vec{p})$ based on Σ_{t_0} as that parametrization for which each point of the moving surface has at each time its velocity perpendicular to the surface on which it lies at that time. This is tantamount to the

requirements that $\vec{R}^{\perp}(t_0,\vec{p}) = \vec{p}$ for every $\vec{p} \in \Sigma_{t_0}$ and that $\frac{\partial \vec{R}^{\perp}}{\partial t}(t,\vec{p})$ be perpendicular to Σ_t at $\vec{R}^{\perp}(t,\vec{p})$ for every t and $\vec{p} \in \Sigma_{t_0}$. (Naturally in general $\vec{R}^{\perp}(t,\vec{p}) \neq \vec{p}$ when $t \neq t_0$.) We will now study the rate of change of the unit normal and local area in the normal parametrization. For simplicity we put $t_0 = 0$. Let $\bar{u} \in T_{\vec{p}}(\Sigma_0)$ and define a "normally convected" tangent vector $\bar{U}(t)$ by

$$\bar{U}(t) = (\vec{R}^{\perp}_t)_{*\vec{p}}(\bar{u}) \tag{1.23}$$

where $(\vec{R}^{\perp}_t)_{*\vec{p}}$ is the differential of $\vec{R}_t$ at the point $\vec{p}$ (see eq. (1.21)). Given a coordinate system (ξ^1,ξ^2) on a neighborhood of $\vec{p}$ in Σ_0, with $\bar{u} = u^1\frac{\partial \vec{R}}{\partial \xi^1}(0,\vec{p}) + u^2\frac{\partial \vec{R}}{\partial \xi^2}(0,\vec{p})$, we have

$$\bar{U}(t) = u^1\frac{\partial \vec{R}}{\partial \xi^1}(t,\vec{p}) + u^2\frac{\partial \vec{R}}{\partial \xi^2}(t,\vec{p})$$

so that

$$\frac{d\bar{U}}{dt} = u^1\frac{\partial}{\partial \xi^1}\frac{\partial \vec{R}^{\perp}}{\partial t} + u^2\frac{\partial}{\partial \xi^2}\frac{\partial \vec{R}^{\perp}}{\partial t}$$

from which

$$\left.\frac{d\bar{U}}{dt}\right|_{t=0} = D_{\bar{u}}(v^{\perp}\vec{n}) = \bar{u}\cdot \mathrm{Grad}\, v^{\perp}\,\vec{n} - v^{\perp}S(\bar{u}) \tag{1.24}$$

where use has been made of eq.(1.10). This is the basic relation from which local rates of deformation in the normal parametrization may be extracted. Let $(\bar{u}_1,\bar{u}_2)$ be an orthonormal basis at $\vec{p}$ with $\vec{n} = \bar{u}_1\times\bar{u}_2$ and $\bar{U}_1(t)$ and $\bar{U}_2(t)$ be defined by "normal convection" of $\bar{u}_1$ and $\bar{u}_2$ as $\bar{U}(t)$ in eq.(1.23). If $J_{\perp}(t,\vec{p})$ is the jacobian of $\vec{R}^{\perp}_t$ at $\vec{p} \in \Sigma_0$ and $\vec{n}_{\vec{q}}(t)$ is the unit normal to Σ_t at $\vec{R}^{\perp}(t,\vec{p})$, we have

$$\vec{n}_{\vec{q}}(t) = J_{\perp}^{-1}(t,\vec{p})\,\bar{U}_1(t)\times\bar{U}_2(t)$$

from which, using eq.(1.24) and $J_{\perp}(0,\vec{p}) = 1$, we get

$$\frac{d\,\vec{n}_{\vec{q}}}{dt}\Big|_{t=0} = \frac{\partial J_\perp^{-1}}{\partial t}\Big|_{t=0}\vec{n} - v^\perp[S(\bar{u}_1)\times\bar{u}_2 + \bar{u}_1\times S(\bar{u}_2)]$$

$$+(\bar{u}_1\cdot \mathrm{Grad}\, v^\perp)\,\vec{n}\times\bar{u}_2 + \bar{u}_2\cdot \mathrm{Grad}\, v^\perp\,\bar{u}_1\times\vec{n}$$

$$= -\left(\frac{\partial J_\perp}{\partial t}\Big|_{t=0} + v^\perp 2H\right)\vec{n} - \mathrm{Grad}\, v^\perp \quad .$$

Since $\frac{d\,\vec{n}_{\vec{q}}}{dt}\Big|_{t=0}$ is tangent to Σ_θ, it follows that

$$\frac{\partial J_\perp}{\partial t}\Big|_{t=0} = -2Hv^\perp \tag{1.25}$$

and $$\frac{d^\perp\vec{n}}{dt} = -\,\mathrm{Grad}\, v^\perp \quad . \tag{1.26}$$

These two formulas are remarkably simple. The first one gives the instantaneous rate of change of area of a small piece of surface whose points are propagating according to the normal parametrization. This follows from the geometrical interpretation of the jacobian derived from eq.(1.22). The second one relates the rate of change of the unit normal along a "normal" trajectory to the normal velocity gradient in a most direct and intuitively satisfying way.

Finally if $\vec{r}(t)$ is any trajectory such that $\vec{r}(t) \in \Sigma_t$ for every t, and $\vec{n}_{\vec{r}}(t)$ is the unit normal to Σ_t at $\vec{r}(t)$, it follows from eqs.(1.19) and (1.26) that

$$\frac{d\,\vec{n}_{\vec{r}}}{dt} = -\,\mathrm{Grad}\, v^\perp - S(\dot{\vec{r}}_{/\!/}) \qquad \text{where } \dot{\vec{r}}_{/\!/} = P(\dot{\vec{r}}) \quad . \tag{1.27}$$

Hereafter the symbol "Grad" will be used exclusively for functions defined on Σ and the symbol "Div" only for tangent vector fields on Σ, in the sense of eqs.(1.3) and (1.6) .

2) A minimal empirical theory of the generic surface balance equation .

This section will serve as a reference frame for subsequent discussions. Its purpose is to establish a general surface balance equation for a two-phase fluid system at a completely empirical level, with the minimum number of assumptions. The essential results are summarized in eqs.(2.19)-(2.24). The eventual originality of this derivation lies in the economy of assumptions and in the obtainment of a functional form of the line flux (eq.(2.18)) which, to our knowledge , has not been reported before.

It is assumed that the interface can be modeled by a region of zero thickness, a true surface , on which surface densities and current densities are postulated. The theory is termed "minimal" for two reasons. First because we do not adopt any specific interpretation for the surface quantities in terms of the diffuse structure of a real interface.(This will come later.) Secondly because we attribute a priori no tangential velocity to the surface Σ_t representing the interface. But of course, just as with any other surface, the moment we assume that it exists (be it only conceptually) and that it moves, it follows from the considerations of the preceding section that at each time it has, at each of its points, a uniquely defined normal speed $v^{\perp}$. On the other hand, to accept a priori a notion of tangential velocity (with presumed physical meaning) for the points of Σ_t would amount to attributing more or less permanent labels to them. Although ob-

viously nothing prevents such labeling in a purely formal or mathematical sense, in order to have *physical* meaning it would have to be based on some physical picture such as Σ_t being material or being a membrane. But since our aim in this section is precisely to isolate or define a general empirical framework free of any such special assumptions, we must refrain from using the concept of a physical tangential velocity of Σ_t as a primitive concept. So it will not enter into our formulation of the basic assumptions below.

Because of the small number of assumptions, the results derived in this section will be quite general. They will serve as a kind of frame of reference for our discussion of existing phenomenological theories in the next sections, as well as for the development of the theory of Chapter III, where a specific interpretation of the surface quantities will be adopted and investigated in considerable detail.

Consider a non-equilibrium two-phase system. The interface (at time t) is represented by a surface Σ_t coinciding with the phase boundary which will be assumed to be macroscopically sharply defined. The surface Σ_t divides the material into two regions M_t^+ and M_t^-, both containing Σ_t for convenience, that is $M_t^+ \cap M_t^- = \Sigma_t$, (the symbol "$\cap$" stands for the intersection of two point-sets, that is the set of all points that lie in both sets) and the unit normal $\vec{n}$ to Σ_t pointing towards M_t^+. According to the continuum or "smoothed" description of matter, the fluid is endowed with various extensive attributes, the amount, flow and internal production of which may be computed using appropriate densities, in the

bulk regions. If V is a region fixed in space not intersecting Σ_t, the total amount of attribute A in V, $A(V)$, its flow $\Phi(\partial V)$ through the boundary ∂V and its internal production rate $P(V)$ are given by

$$A(V) = \int_V a \, dV \tag{2.1}$$

$$\Phi(\partial V) = \int_{\partial V} \vec{J} \cdot \vec{N} \, dA \tag{2.2}$$

$$P(V) = \int_V \sigma \, dV \tag{2.3}$$

where a, $\vec{J}$ and σ are the bulk density, current density and internal production density respectively. These three quantities will be hereafter collectively refered to as "densities". At the interface the densities associated with some attributes may have discontinuities in the form of jumps. We will denote by a^+ (resp. a^-) the function defined on M_t^+ (resp. M_t^-) and equal to a in M_t^+ (resp. M_t^-) deprived of Σ_t and to the limiting value of a from the + (resp. the -) side of Σ_t, at each point of Σ_t. When the density a has a jump at a point $\vec{p}$ of Σ_t, the choice of the value $a(\vec{p})$ is quite arbitrary and in any case is physically irrelevant. We shall adopt the convention that $a(\vec{p}) = a^+(\vec{p})$ at every $\vec{p} \in \Sigma_t$. The same notations and convention will be adopted for $\vec{J}$ and σ. Following the notations of Vodák [1978], the jumps at the interface will be denoted by double square brackets:

$$\begin{aligned} [\![a]\!](\vec{p}) &\equiv a^+(\vec{p}) - a^-(\vec{p}) \\ [\![\sigma]\!](\vec{p}) &\equiv \sigma^+(\vec{p}) - \sigma^-(\vec{p}) \\ [\![\vec{J}]\!](\vec{p}) &\equiv \vec{J}^+(\vec{p}) - \vec{J}^-(\vec{p}) \end{aligned} \tag{2.4}$$

for every $\vec{p} \in \Sigma_t$. Next we postulate that, when a *fixed* region V intersects the interface, the total amount of attribute A in V, denoted by $A^*(V)$, is expressible as

$$A^*(V) = \int_V a \, dV + \int_{\Sigma_t(V)} a^S \, dA \qquad (2.5)$$

where a is the same bulk A-density as above, a^S is a surface excess density defined on Σ_t, and $\Sigma_t(V) = V \cap \Sigma_t$ is the patch of Σ_t contained in the fixed region V at time t. Equation (2.5) may be considered as the general expression for the total amount of A, valid whether V intersects Σ or not, if the surface integral is set by definition equal to zero when $V \cap \Sigma_t$ is empty. Likewise the rate of internal production is assumed to be expressible as

$$P^*(V) = \int_V \sigma \, dV + \int_{\Sigma_t(V)} \sigma^S \, dA \quad . \qquad (2.6)$$

Finally we postulate a surface current density $\vec{j}$ defined on Σ_t and such that when a *fixed* surface S, with unit normal vector field $\vec{N}$, meets Σ_t *at right angle* all along the curve $S \cap \Sigma_t$ then the net rate of transfer of A through S is

$$\Phi^*(S) = \int_S \vec{J} \cdot \vec{N} \, dA + \int_{S \cap \Sigma_t} \vec{j} \cdot \vec{N} \, d\lambda \qquad (2.7)$$

where $\vec{J}$ is the bulk current density and $d\lambda$ is the arc-length element on the curve $S \cap \Sigma_t$. If the surface S meets Σ_t, but not at right angle, then we write

$$\Phi^*(S) = \int_S \vec{J} \cdot \vec{N} \, dA + \int_{S \cap \Sigma_t} (\vec{j} \cdot \vec{\nu} + \Delta) \, d\lambda \quad , \qquad (2.8)$$

where at any $\vec{p} \in S \cap \Sigma_t$, $\bar{\nu}$ is the normalized projection of $\vec{N}$ on $T_{\vec{p}}(\Sigma_t)$ (see Fig. 1), and the explicit form of Δ has yet to be found. All that is assumed at this point is that Δ vanishes at any point of $S \cap \Sigma_t$ where $\vec{N} \cdot \vec{n}$ vanishes, or equivalently where $\vec{N} = \bar{\nu}$.

The general balance equation postulated reads naturally in nonlocal form ,

$$\frac{d}{dt} A^*(V) + \Phi^*(\partial V) - P^*(V) = 0 \qquad (2.9)$$

where V is any region fixed in space. For this to hold for every region V not intersecting the interface at time t, it is necessary and sufficient that the usual bulk balance equation

$$\frac{\partial a}{\partial t} + \nabla \cdot \vec{J} - \sigma = 0 \qquad (2.10)$$

be satisfied at every point not on Σ_t. We note that spatial or time derivatives are nowhere meant in the sense of distribution theory in this work, so that eq.(2.10) is used only at points not lying on Σ_t. It will happen that expressions like $\nabla \cdot \vec{J}$, which may be undefined on Σ_t, appear as parts of integrands in integrals over regions containing part of Σ_t. Their lack of definition over these sets is however clearly immaterial because these sets are of (three-dimensional) measure zero.

Consider a *motionless* region V intersecting the interface Σ_t at time t and extending into M_t^+ and M_t^-, as illustrated in Fig. 1. Our task is now to evaluate the terms of eq.(2.9) for this type of region. First it is easily seen that

$$\frac{d}{dt}\int_V a \, dV = \int_{V_t^+} \frac{\partial a^+}{\partial t} \, dV + \int_{V_t^-} \frac{\partial a^-}{\partial t} \, dV - \int_{\Sigma_t(V)} [\![a]\!] v^{\perp} \, dA \qquad (2.11)$$

where $V_t^{\pm} = V \cap M_t^{\pm}$, $[\![a]\!]$ is defined by eq.(2.4), and $v^{\perp}$ is the normal speed of Σ_t defined by eq.(1.16). To compute $\frac{d}{dt} A^*(V)$ we also need the time derivative of the second integral in eq.(2.5). At the end of this section we shall prove that it is given by

$$\frac{d}{dt}\int_{\Sigma_t(V)} a^S \, dA = \int_{\Sigma_t(V)} [\frac{d^{\perp} a^S}{dt} - 2Hv^{\perp}a^S] \, dA - \int_{L_t(\partial V)} \tau v^{\perp} a^S \, d\lambda \qquad (2.12)$$

The meaning of the various terms occuring in this equation are as follows (see Fig. 1). $\Sigma_t(V) = V \cap \Sigma_t$ is the part of Σ_t contained in V and dA is the area element on Σ_t. The derivative $\frac{d^{\perp}}{dt}$ is the normal time derivative defined by eq.(1.17), H is the mean curvature function of Σ_t (defined by eq.(1.13)), and $v^{\perp}$ is the normal speed of Σ_t defined by eq.(1.16). $L_t(\partial V)$ is the curve bounding the patch $\Sigma_t(V)$ or equivalently is the curve along which ∂V meets with Σ_t. At each point $\vec{p}$ of this curve, the geometrical factor τ is defined by

$$\tau \equiv \frac{\vec{N}\cdot\vec{n}}{\vec{N}\cdot\bar{\nu}} = \operatorname{cotan}(\widehat{\vec{N},\vec{n}}) \qquad (2.13)$$

where $\vec{N}$ is the outward unit normal to ∂V, $\bar{\nu}$ is the normalized projection of $\vec{N}$ on $T_{\vec{p}}(\Sigma_t)$, $\vec{n}$ is the unit normal to Σ_t, $(\widehat{\vec{N},\vec{n}})$ is the angle between $\vec{N}$ and $\vec{n}$, and $d\lambda$ is the arc-length element on $L_t(\partial V)$.

Now according to eq.(2.8), the second term in eq.(2.9) is given by

$$\begin{aligned}\Phi^*(\partial V) &= \int_{\partial V} \vec{J}\cdot\vec{N} \, dA + \int_{L_t(\partial V)} (\bar{J}\cdot\bar{\nu} + \Delta) \, d\lambda \\ &= \int_{V_t^+} \nabla\cdot\vec{J}^+ \, dV + \int_{V_t^-} \nabla\cdot\vec{J}^- \, dV + \int_{\Sigma_t(\partial V)} \{[\![\vec{J}\cdot\vec{n}]\!] + \operatorname{Div}\bar{J}\} \, dA + \int_{L_t(\partial V)} \Delta \, d\lambda \, ,\end{aligned} \qquad (2.14)$$

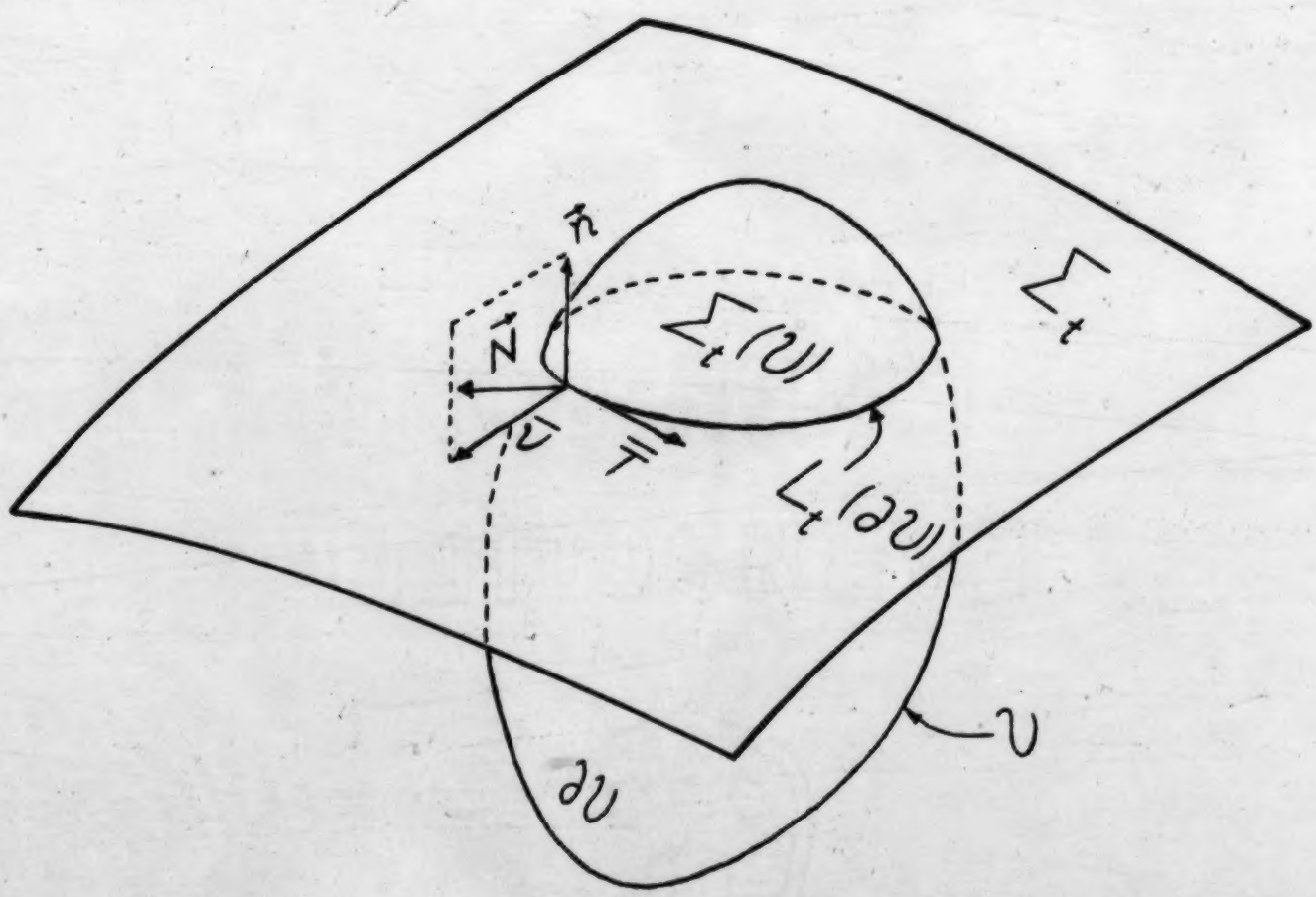

Figure 1: The dividing surface Σ_t intersecting a three-dimensional region V fixed in space, with boundary ∂V and outward unit normal vector $\vec{N}$.

where use has been made of the divergence theorem in three and two dimensions.

Combining this with eqs.(2.5), (2.11), (2.12) and (2.6), eq.(2.9) may be rewritten as

$$\int_{V_t^+} (\frac{\partial a^+}{\partial t} + \nabla\cdot\vec{J}^+ - \sigma^+)\, dV + \int_{V_t^-} (\frac{\partial a^-}{\partial t} + \nabla\cdot\vec{J}^- - \sigma^-)\, dV$$

$$+ \int_{\Sigma_t(V)} \{\frac{d^\perp a^s}{dt} - 2Hv^\perp a^s + \mathrm{Div}\,\vec{j} - \sigma^s + [\![\vec{J}\cdot\vec{n} - av^\perp]\!]\}\, dA$$

$$+ \int_{L_t(\partial V)} (\Delta - \tau a^s v^\perp)\, d\lambda = 0 .$$

But the first two integrals vanish because of eq.(2.10) and the equation reduces to

$$\int_{\Sigma_t(V)} \{\frac{d^\perp a^s}{dt} - 2Hv^\perp a^s + \mathrm{Div}\,\vec{j} - \sigma^s + [\![\vec{J}\cdot\vec{n} - av^\perp]\!]\}\, dA$$

$$+ \int_{L_t(\partial V)} (\Delta - \tau a^s v^\perp)\, d\lambda = 0 . \qquad (2.15)$$

When V is so chosen that ∂V meets Σ_t at right angle all along the curve $L_t(\partial V)$, the second integral vanishes and the arbitrariness remaining in the choice of V suffices to imply the vanishing of the first integrand. This gives the surface balance equation

$$\frac{d^\perp a^s}{dt} - 2Hv^\perp a^s + \mathrm{Div}\,\vec{j} - \sigma^s + [\![\vec{J}\cdot\vec{n} - av^\perp]\!] = 0 . \qquad (2.16)$$

Coming back to equation (2.15) we now have, for an arbitrary fixed region V intersecting Σ_t

$$\int_{L_t(\partial V)} (\Delta - \tau a^s v^\perp)\, d\lambda = 0 . \qquad (2.17)$$

The function Δ occurring in eq.(2.8) could a priori depend on any property of the surface S defined along the curve $S\cap\Sigma_t$. However substituting for V in eq.(2.17) a special region such that part of ∂V coincides with S and the rest meets Σ_t at right angle, we get

$$\int_\Gamma (\Delta - \tau a^S v^\perp)\, d\lambda = 0$$

where $\Gamma = S\cap\Sigma_t$. A little thought reveals that the same equation must hold for any arbitrarily small portion of Γ so that Δ must equal $\tau a^S v^\perp$. Hence eq.(2.8) becomes

$$\Phi^*(S) = \int_S \vec{J}\cdot\vec{n}\, dA + \int_{S\cap\Sigma_t} (\bar{j}\cdot\bar{\nu} + \tau j^\perp)\, d\lambda \qquad (2.18)$$

where $j^\perp = a^S v^\perp$.

For future reference we will collect the important equations :

$$A^*(V) = \int_V a\, dV + \int_{\Sigma_t(V)} a^S\, dA \qquad (2.19)$$

$$P^*(V) = \int_V \sigma\, dV + \int_{\Sigma_t(V)} \sigma^S\, dA \qquad (2.20)$$

$$\Phi^*(\partial V) = \int_{\partial V} \vec{J}\cdot\vec{N}\, dA + \int_{L_t(\partial V)} (\bar{j}\cdot\bar{\nu} + \tau j^\perp)\, d\lambda \qquad (2.21)$$

$$j^\perp = a^S v^\perp \quad , \quad \tau = \frac{\vec{N}\cdot\vec{n}}{\vec{N}\cdot\bar{\nu}} \qquad (2.22)$$

$$\frac{\partial a}{\partial t} + \nabla\cdot\vec{J} - \sigma = 0 \quad \text{(at points not on } \Sigma_t) \qquad (2.23)$$

$$\frac{d^\perp a^S}{dt} - 2Hv^\perp a^S + \mathrm{Div}\,\bar{j} - \sigma^S + [\![\vec{J}\cdot\vec{n} - av^\perp]\!] = 0 \qquad (2.24)$$

As far as we know, the contribution $\tau j^\perp = \tau a^S v^\perp$ to the line flux integrand in eq.(2.21) has not been reported before.

Equations (2.23) and (2.24) express the balance of a scalar quantity. The general balance equations for a vector quantity may be easily deduced from them. Consider a vector-valued extensive attribute $\vec{A}$ with bulk and surface densities $\vec{a}$, $\vec{\sigma}$, $\vec{a}^S$ and $\vec{\sigma}^S$. Equations (2.19) and (2.20) still hold for vector densities. The flux density in the bulk will, as in the scalar case $(\vec{J}\cdot\vec{N})$, be a linear but this time vector-valued function of $\vec{N}$, so that the bulk contribution to the flux will be

$$\vec{\Phi}(\partial V) = \int_{\partial V} M^*(\vec{N})\, dA \qquad (2.25)$$

where M is a field of linear operators and the adjoint has been taken for subsequent notational convenience. In eq. (2.21), the term $\tau j^{\perp} = \tau v^{\perp}\vec{a}^S$ will be replaced by $\tau v^{\perp}\vec{a}^S$. As in the scalar case $(\bar{j}\cdot\bar{\nu})$, the line flux density will be a linear but this time vector-valued function of $\bar{\nu}$, $Q(\bar{\nu})$, so that the surface contribution to the flux will be

$$\int_{L_t(\partial V)} (Q(\bar{\nu}) + \tau v^{\perp}\vec{a}^S)\, d\lambda \quad .$$

At each point $\vec{p} \in \Sigma$, $Q_{\vec{p}}$ is a linear map from $T_{\vec{p}}(\Sigma_t)$ into E_3. Decomposing $Q_{\vec{p}}(\bar{u})$ into normal and tangential parts it follows that at each $\vec{p} \in \Sigma_t$ there exists a unique vector $\bar{\Gamma}_{\vec{p}} \in T_{\vec{p}}(\Sigma_t)$ and a unique linear operator $M^S_{\vec{p}} : T_{\vec{p}}(\Sigma_t) \to T_{\vec{p}}(\Sigma_t)$ such that

$$Q_{\vec{p}}(\bar{u}) = (M^S_{\vec{p}})^*(\bar{u}) + \bar{\Gamma}_{\vec{p}}\cdot\bar{u}\,\vec{n} \qquad (2.26)$$

for every $\bar{u} \in T_{\vec{p}}(\Sigma_t)$, where the adjoint has been taken for later notational convenience. Combining this with eq. (2.25) we see that the general expression for the flux in the vector case is

$$\vec{\Phi}^*(\partial V) = \int_{\partial V} M^*(\vec{N})\, dA + \int_{L_t(\partial V)} [(M^S)^*(\bar{\nu}) + \bar{\Gamma}\cdot\bar{\nu}\,\vec{n} + \tau v^{\perp}\vec{a}^S]\, d\lambda \qquad (2.27)$$

where again the second integral vanishes by definition when Σ_t and ∂V do not intersect. It follows that, if $\vec{e}$ is a constant vector, the flux associated to the scalar attribute $\vec{e}\cdot\vec{A}$ will be

$$\vec{e}\cdot\vec{\Phi}^*(\partial V) = \int_{\partial V} \vec{e}\cdot M^*(\vec{N})\, dA + \int_{L_t(\partial V)} [\vec{e}\cdot(M^S)^*(\bar{\nu}) + \vec{e}\cdot\vec{n}\,\bar{\Gamma}\cdot\bar{\nu} + \tau v^{\perp}\vec{e}\cdot\vec{a}^S]\, d\lambda$$

$$= \int_{\partial V} M(\vec{e})\cdot\vec{N}\, dA + \int_{L_t(\partial V)} [(M^S(\bar{e}) + \vec{e}\cdot\vec{n}\,\bar{\Gamma})\cdot\bar{\nu} + \tau v^{\perp}\vec{e}\cdot\vec{a}^S]\, d\lambda$$

where $\bar{e} \equiv P(\vec{e})$, so that the bulk current density associated to the scalar density $\vec{e}\cdot\vec{a}$ is $M(\vec{e})$ and the surface current density associated to $\vec{e}\cdot\vec{a}^S$ is $M^S(\bar{e}) + \vec{e}\cdot\vec{n}\,\bar{\Gamma}$. It follows that the bulk balance equation for $\vec{e}\cdot\vec{a}$ is

$$\frac{\partial(\vec{e}\cdot\vec{a})}{\partial t} + \nabla\cdot[M(\vec{e})] - \vec{e}\cdot\vec{\sigma} = 0$$

which, since $\nabla\cdot[M(\vec{e})] = (\nabla\cdot M)\cdot\vec{e} + \mathrm{Tr}(M\nabla\vec{e}) = (\nabla\cdot M)\cdot\vec{e}$ and since $\vec{e}$ is arbitrary, implies that

$$\frac{\partial\vec{a}}{\partial t} + \nabla\cdot M - \vec{\sigma} = \vec{0}\ . \tag{2.28}$$

This is the general balance equation for a bulk vector-valued density. It follows also that the surface balance equation for the scalar $\vec{e}\cdot\vec{a}^S$ is

$$\frac{d^{\perp}(\vec{e}\cdot\vec{a}^S)}{dt} - 2Hv^{\perp}\vec{e}\cdot\vec{a}^S + \mathrm{Div}[M^S(\bar{e}) + \vec{e}\cdot\vec{n}\,\bar{\Gamma}] - \vec{e}\cdot\vec{\sigma}^S + [\![\vec{n}\cdot M(\vec{e}) - \vec{e}\cdot\vec{a}\,v^{\perp}]\!] = 0 \tag{2.29}$$

Now we have from eqs.(1.9) and (1.15)

$$\mathrm{Div}[M^S(\bar{e})] = (\mathrm{Div}M^S)\cdot\bar{e} + \overline{\mathrm{Tr}}(M^S\,\bar{\nabla}\bar{e})$$

$$= (\mathrm{Div}M^S)\cdot\vec{e} + \vec{n}\cdot\vec{e}\,\overline{\mathrm{Tr}}(M^S S)$$

$$= \vec{e}\cdot[\mathrm{Div}M^S + \overline{\mathrm{Tr}}(SM^S)\,\vec{n}]$$

while on the other hand

$$\mathrm{Div}(\vec{e}\cdot\vec{n}\,\bar{\Gamma}) = \vec{e}\cdot\vec{n}\,\mathrm{Div}\,\bar{\Gamma} + \bar{\Gamma}\cdot\mathrm{Grad}\,\vec{e}\cdot\vec{n}$$

But in general

$$\bar{u}\cdot\mathrm{Grad}\,(\vec{e}\cdot\vec{n}) = D_{\bar{u}}(\vec{e}\cdot\vec{n}) = \vec{e}\cdot D_{\bar{u}}\vec{n} = -\vec{e}\cdot S(\bar{u})$$
$$= -\bar{e}\cdot S(\bar{u}) = -S(\bar{e})\cdot\bar{u}$$

where $\bar{e} \equiv P(\vec{e})$ and use has been made of eqs.(1.3), (1.10) and (1.11), so that

$$\mathrm{Grad}\,(\vec{e}\cdot\vec{n}) = -S(\bar{e})\ . \tag{2.30}$$

It follows that

$$\bar{\Gamma}\cdot\mathrm{Grad}\,(\vec{e}\cdot\vec{n}) = -\bar{\Gamma}\cdot S(\bar{e}) = -S(\bar{\Gamma})\cdot\bar{e} = -S(\bar{\Gamma})\cdot\vec{e}$$

from which

$$\mathrm{Div}\,(\vec{e}\cdot\vec{n}\,\bar{\Gamma}) = \vec{e}\cdot[-S(\bar{\Gamma}) + (\mathrm{Div}\,\bar{\Gamma})\,\vec{n}]\ .$$

Substituting these results in eq.(2.29) and invoking the arbitrariness of $\vec{e}$, we get

$$\frac{d^{\perp}\vec{a}^{S}}{dt} - 2Hv^{\perp}\vec{a}^{S} + \mathrm{Div}M^{S} + \overline{\mathrm{Tr}}(SM^{S})\,\vec{n} + (\mathrm{Div}\,\bar{\Gamma})\,\vec{n}$$
$$- S(\bar{\Gamma}) - \vec{\sigma}^{S} + [\![M^{*}(\vec{n}) - v^{\perp}\vec{a}]\!] = \vec{0}\ . \tag{2.31}$$

This is the general surface balance equation for vector-valued densities. To get an intuitive understanding of the terms involving M^S and $\bar{\Gamma}$, we note that if γ_ε is a family of simple closed arcs traced out on Σ_t around a point $\vec{p}$, with enclosed area s_ε such that $s_\varepsilon \to 0$ as $\varepsilon \to 0$, then

$$\lim_{\varepsilon\to 0}\frac{1}{s_\varepsilon}\int_{\gamma_\varepsilon} Q(\bar{\nu})\,d\lambda = \lim_{\varepsilon\to 0}\frac{1}{s_\varepsilon}\int_{\gamma_\varepsilon}[(M^{S})^{*}(\bar{\nu}) + \bar{\Gamma}\cdot\bar{\nu}\,\vec{n}]\,d\lambda$$
$$= \mathrm{Div}M^{S} + \overline{\mathrm{Tr}}(SM^{S})\,\vec{n} + (\mathrm{Div}\,\bar{\Gamma})\,\vec{n} - S(\bar{\Gamma})$$

(this last expression being evaluated at $\vec{p}$).

Equation (2.26) may be rewritten as $Q = (M^S)^* + \vec{n}\otimes\bar{\Gamma}$,

where in general, given two vectors $\vec{A},\vec{B}$, $\vec{A}\otimes\vec{B}$ is the linear operator defined by $\vec{A}\otimes\vec{B}(\vec{u}) = (\vec{B}\cdot\vec{u})\vec{A}$ for every $\vec{u} \in E_3$. For convenience we bring together all equations pertaining to the vector case:

$$\vec{A}^*(V) = \int_V \vec{a}\, dV + \int_{\Sigma_t(V)} \vec{a}^S\, dA\ ,\ \vec{P}^*(V) = \int_V \vec{\sigma}\, dV + \int_{\Sigma_t(V)} \vec{\sigma}^S\, dA \tag{2.32}$$

$$\vec{\Phi}^*(V) = \int_{\partial V} M^*(\vec{N})\, dA + \int_{L_t(\partial V)} [Q(\bar{v}) + \tau v^{\perp}\vec{a}^S]\, d\lambda \tag{2.33}$$

$$Q = (M^S)^* + \vec{n}\otimes\bar{\Gamma} \qquad (PM^S = M^S,\ \vec{n}\cdot\bar{\Gamma} = 0) \tag{2.34}$$

$$\frac{\partial\vec{a}}{\partial t} + \nabla\cdot\vec{M} - \vec{\sigma} = \vec{0} \tag{2.35}$$

$$\frac{d^{\perp}\vec{a}^S}{dt} - 2Hv^{\perp}\vec{a}^S + \mathrm{Div}M^S + \overline{\mathrm{Tr}}(SM^S)\,\vec{n} + (\mathrm{Div}\,\bar{\Gamma})\,\vec{n} - S(\bar{\Gamma}) - \vec{\sigma}^S + [\![M^*(\vec{n}) - v^{\perp}\vec{a}]\!] = \vec{0}. \tag{2.36}$$

In concluding this section, we will prove eq.(2.12) which is instrumental in many of our derivations. Although related equations appear in the literature, as for instance in (Moeckel [1975]), we could not find a proof, nor even a statement of the specific result embodied in eq.(2.12).

Let Σ^0 be a surface fixed in space and S_t be a piece of surface moving about in Σ^0. Given at time dependent function $\vec{p} \to f(\vec{p},t)$ defined on Σ^0, it is easy to show that

$$\frac{d}{dt}\int_{S_t} f\, dA = \int_{S_t} \frac{\partial f}{\partial t}\, dA \int_{\partial S_t} f v_\nu\, d\lambda\ , \tag{2.37}$$

where v_ν is the outward normal velocity of the boundary curve ∂S_t (this velocity is the obvious analogue, for a curve moving on a surface, of the normal velocity of a surface moving in space, as

defined in Section 1). We shall obtain a result actually slightly more general than eq.(2.12) in that we shall find the rate of change of the integral

$$I(t) = \int_{U_t \cap \Sigma_t} \alpha \, dA \quad , \tag{2.38}$$

where α is a function defined on the moving surface Σ_t (that is a function α_t is defined on each Σ_t), U_t is a possibly changing volume contained within some closed surface ∂U_t the points of which move according to some specified velocity distribution $\vec{V}_t$, and $U_t \cap \Sigma_t$ is the patch of Σ_t contained in U_t. The points in the interior of U_t need not be attributed any specific velocities as this is completely irrelevant to the integral in eq.(2.38). It is also intuitively obvious that only the component of $\vec{V}_t$ normal to ∂U_t should be involved in computing $\frac{dI}{dt}$. We will use the normal parametrization based on Σ_t, $\vec{R}^{\perp}_{\tau}$, introduced at the end of Section 1. We recall that it is defined by

$$\vec{R}^{\perp}_{\tau} : \Sigma_t \to \Sigma_{t+\tau} : \vec{p} \to \vec{R}^{\perp}_{\tau}(\vec{p}) \equiv \vec{R}^{\perp}(\tau, \vec{p})$$

where the function $\vec{R}^{\perp}(\tau, \vec{p})$ is such that $\vec{R}^{\perp}(0, \vec{p}) = \vec{p}$ for every $\vec{p} \in \Sigma_t$, and $\frac{\partial \vec{R}^{\perp}}{\partial \tau}(\tau, \vec{p})$ is perpendicular to $\Sigma_{t+\tau}$ at $\vec{R}^{\perp}(\tau, \vec{p})$. In order to use this parametrization, we start by noting the obvious equality

$$\frac{d}{dt'} \int_{U_{t'} \cap \Sigma_{t'}} \alpha \, dA \Bigg|_{t'=t} = \frac{d}{d\tau} \int_{U_{t+\tau} \cap \Sigma_{t+\tau}} \alpha(t+\tau, \vec{p}) \, dA \Bigg|_{\tau=0} \quad . \tag{2.39}$$

Let us denote by S_τ the patch $U_{t+\tau} \cap \Sigma_{t+\tau}$ at time $t+\tau$ and by S^*_τ the

region of Σ_t which is mapped into S_τ by $\vec{R}^\perp_\tau$, that is $S^* = (\vec{R}^\perp_\tau)^{-1}(S_\tau)$. From eq.(1.22), it follows that

$$\int_{S_\tau} \alpha(t+\tau,\vec{p})\, dA = \int_{S^*_\tau} \alpha(t+\tau,\vec{R}^\perp(\vec{q}))\, J_\perp(\tau,\vec{q})\, dA ,$$

where $J_\perp$ is the jacobian of the normal parametrization. Combining this with eqs.(2.37),(2.38) and (2.39) yields

$$\frac{dI}{dt}(t) = \int_{S^*_0} \frac{\partial}{\partial\tau}[\alpha(t+\tau,\vec{R}^\perp_\tau(\vec{q}))\, J_\perp(\tau,\vec{q})\Big|_{\tau=0} dA + \int_{\partial S^*_0} \alpha v_\nu\, d\lambda$$

$$= \int_{U_t\cap\Sigma_t} [\frac{d^\perp\alpha}{dt} - 2Hv^\perp\alpha]\, dA + \int_{\partial S^*_0} \alpha v_\nu\, d\lambda , \qquad (2.40)$$

where use has been made of eq.(1.25) together with the fact that $\vec{R}^\perp_0$ is the identity map on Σ_t, so that $S^*_0 = U_t\cap\Sigma_t$. All that remains to be done is to compute the normal velocity v_ν in the second integral in eq.(2.40). The curve ∂S^0_τ is a closed curve moving, as τ evolves, in the fixed reference configuration Σ_t. Let $\xi \to \vec{q}(\xi,\tau)$ be a parametrization of this curve at time τ. By the very definition of the normal velocity v_ν we have

$$\frac{\partial\vec{q}}{\partial\tau} = \left(\frac{\partial\vec{q}}{\partial\tau}\right)_{//} + v_\nu\bar{\nu}$$

where $\bar{\nu}$ has its usual meaning (outward unit normal to ∂S^*_τ, tangent to Σ_t) and $\bar{\nu}\cdot\left(\frac{\partial\vec{q}}{\partial\tau}\right)_{//} = 0$. At fixed ξ, $\vec{R}^\perp(\tau,\vec{q}(\xi,\tau))$ is a point of the curve on which $\partial U_{t+\tau}$ and $\Sigma_{t+\tau}$ intersect, and the velocity of this point is

$$\frac{\partial}{\partial\tau}\vec{R}^\perp(\tau,\vec{q}(\xi,\tau))]\Big|_\xi = \frac{\partial\vec{R}^\perp}{\partial\tau}(\tau,\vec{q}(\xi,\tau)) + (\vec{R}^\perp_\tau)_*(\frac{\partial\vec{q}}{\partial\tau}(\xi,\tau))$$

$$= v^{\perp}\vec{n} + (\vec{R}^{\perp}_{\tau})_{*}\left[\left(\frac{\partial \vec{q}}{\partial \tau}\right)_{//}\right] + v_{\nu}(\vec{R}^{\perp}_{\tau})_{*}(\bar{v}) \ ,$$

where $(\vec{R}^{\perp}_{\tau})_{*}$ is the differential of $\vec{R}^{\perp}_{\tau}$ (see eq.(1.21)) .

On the other hand, if $\vec{N}$ is the outward unit normal to $\partial U_{t+\tau}$ at the point $\vec{R}^{\perp}(\tau,\vec{q}(\xi,\tau))$, and $V^{\perp}$ is the normal velocity of the surface $\partial U_{t+\tau}$ at that point, then from eq.(1.18),

$$\vec{N}\cdot\frac{\partial}{\partial \tau}[\vec{R}^{\perp}(\tau,\vec{q}(\xi,\tau))] = V^{\perp} \ .$$

Using this together with the previous equation evaluated at time $\tau = 0$ at which $\vec{R}^{\perp}_{\tau}$ is simply the identity map on Σ_t, we get

$$V^{\perp} = v^{\perp}\,\vec{N}\cdot\vec{n} + v_{\nu}\,\vec{N}\cdot\bar{v}$$

where we have used the geometrically evident equation $\vec{N}\cdot\left(\frac{\partial \vec{q}}{\partial \tau}\right)_{//} = 0$.

It follows that

$$v_{\nu} = \frac{V^{\perp}}{\vec{N}\cdot\bar{v}} - \tau v^{\perp}$$

where now $\tau \equiv \frac{\vec{N}\cdot\vec{n}}{\vec{N}\cdot\bar{v}}$ is the geometrical factor introduced in eq. (2.13) and has nothing to do with the time parameter used above. Inserting this expresssion for v_{ν} in eq.(2.40) yields the desired result:

$$\frac{d}{dt}\int_{U_t\cap\Sigma_t}\alpha\,dA = \int_{U_t\cap\Sigma_t}[\frac{d^{\perp}\alpha}{dt} - 2Hv^{\perp}\alpha]\,dA + \int_{\partial(U_t\cap\Sigma_t)}\alpha[\frac{V^{\perp}}{\vec{N}\cdot\bar{v}} - \tau v^{\perp}]\,d\lambda \qquad (2.41)$$

where $\partial(U_t\cap\Sigma_t)$ is the curve bounding the patch $U_t\cap\Sigma_t$. When U_t does not depend on time, that is, is a region V fixed in space, $V^{\perp} = 0$ and eq.(2.41), with our previous notations, reduces to eq.(2.12):

$$\frac{d}{dt}\int_{\Sigma_t(V)}\alpha\,dA = \int_{\Sigma_t(V)}[\frac{d^{\perp}\alpha}{dt} - 2Hv^{\perp}\alpha]\,dA - \int_{L_t(\partial V)}\tau v^{\perp}\alpha\,d\lambda \ . \qquad (2.42)$$

The three terms on the right-hand side correspond to the three causes responsible for the variation of the integral on the left: first the time variation of α along a normal trajectory, secondly the local stretching or contraction of the surface Σ_t(see eq.(1.25)) and thirdly an edge effect due to addition or removal of strips of $\Sigma_t(V)$ to the integration domain as its border is delimited by varying portions of ∂V when Σ_t moves.

The general surface balance equation at the empirical level was given perhaps for the first time by Ghez [1966], although his version is not quite correct because he forgot a contribution from the bulk density jump. Special versions were given earlier by Scriven [1960] and Slattery [1964], while jump conditions in a more restricted sense have long been known (Truesdell [1960]). Derivations of the general surface balance equation at the empirical level have also been given by Moeckel [1975], Deemer and Slattery [1978], Bedeaux et al [1976] and Vodák [1978]. The novel feature of the derivation given in this section is that no reference whatsoever is made to tangential velocities on the dividing surface, in arriving at eq.(2.24). To our knowledge, the result embodied in eq.(2.42) has not been reported before. From our more general standpoint, we may if we wish recover the formulations of other authors, but our formulation can also perfectly accomodate the conception of the dividing surface as merely a conceptual device, in the spirit of the Gibbs approach described in Section 1 of Chapter I. Though of lesser importance, the formalism for vector densities embodied in eqs.(2.32-36) also appears to be original.

3) Mass, momentum and angular momentum balance .

Again for the purpose of future reference, we shall apply the general equations obtained in the previous section to the cases of mass, momentum and angular momentum. The system considered will be one made of n chemically non-reacting constituants, and devoid of internal angular momentum (De Grott and Mazur [1969], p. 305). Here too we are careful to introduce the least possible number of assumptions. For example, in considering the balance of linear momentum, we could argue as if the dividing surface were material and introduce a surface stress tensor in terms of surface forces. We could then write down at once an equation looking just like Newton's second law. In contrast to this, we merely assume the existence of a Q field (see eqs.(2.33) and (2.34)) that gives the surface contribution to the flow of momentum. This is clearly the least that one can assume. The resulting surface momentum balance equation then looks rather abstract. To proceed further and obtain an equation more reminiscent of Newton's second law, we need some properties of the momentum Q field. They could be written down heuristically on the basis of an intuitive "material" picture of the dividing surface. However it turns out that they follow from the balance of angular momentum. We are thus able to show that the intuitively appealing form of the surface momentum balance equation follows from general physical principles and minimal assumptions which do not depend on any specific interpretation of the surface fields in terms of the diffuse structure of the interface.

The bulk and surface densities of the constituant α of the mixture will be denoted by ρ_α and ρ_α^s, with corresponding bulk and surface current densities $\vec{J}_\alpha$ and $\bar{j}_\alpha$. The mass balance equations are then simply from eqs.(2.23) and (2.24)

$$\frac{\partial \rho_\alpha}{\partial t} + \nabla\cdot\vec{J}_\alpha = 0 \tag{3.1}$$

$$\frac{d^\perp \rho_\alpha^s}{dt} - 2Hv^\perp\rho_\alpha^s + \mathrm{Div}\,\bar{j}_\alpha + [\![\vec{J}_\alpha\cdot\vec{n} - \rho_\alpha v^\perp]\!] = 0 . \tag{3.2}$$

Summation over $\alpha = 1,2,\ldots,n$ gives

$$\frac{\partial \rho}{\partial t} + \nabla\cdot\vec{G} = 0 \tag{3.3}$$

$$\frac{d^\perp \rho^s}{dt} - 2Hv^\perp\rho^s + \mathrm{Div}\,\bar{g} + [\![\vec{G}\cdot\vec{n} - \rho v^\perp]\!] = 0 \tag{3.4}$$

where

$$\rho \equiv \sum_{\alpha=1}^{n} \rho_\alpha , \quad \rho^s \equiv \sum_{\alpha=1}^{n} \rho_\alpha^s , \quad \vec{G} \equiv \sum_{\alpha=1}^{n} \vec{J}_\alpha , \quad \bar{g} \equiv \sum_{\alpha=1}^{n} \bar{j}_\alpha . \tag{3.5}$$

We now consider the case of linear momentum. In the bulk regions, the momentum density coincides with the total mass current $\vec{G}$ defined in eq.(3.5). The associated balance equation is then

$$\frac{\partial \vec{G}}{\partial t} + \nabla\cdot\Pi - \vec{F} = \vec{0} \tag{3.6}$$

where Π is the momentum flux density tensor (Landau and Lifshitz [1966]) and $\vec{F}$ the body force per unit volume. The full expression for Π in terms of the bulk stress tensor T would be (Samohýl [1969], Kehlen and Baranowski [1976])

$$\begin{aligned} \Pi &= -T + \sum_{\alpha=1}^{n} \rho_\alpha \vec{w}_\alpha \otimes \vec{w}_\alpha \\ &= -T + \rho\,\vec{w}\otimes\vec{w} + \sum_{\alpha=1}^{n} \rho_\alpha \vec{\omega}_\alpha \otimes \vec{\omega}_\alpha \end{aligned} \tag{3.7}$$

where $\vec{w}_\alpha$ is the bulk velocity of constituant α ($\vec{J}_\alpha = \rho_\alpha \vec{w}_\alpha$), $\vec{w}$ is the bulk barycentric velocity ($\rho\vec{w} = \vec{G}$), and $\vec{\omega}_\alpha \equiv \vec{w}_\alpha - \vec{w}$. In the following we shall neglect the last (diffusional) term in eq.(3.7) as is done in the second chapter of (De Groot and Mazur [1969]). The complete equations could be recovered by considering that the last term in eq.(3.7) has been absorbed in - T. So we shall write

$$\Pi \doteq - T + \rho \vec{w} \otimes \vec{w} \quad . \tag{3.8}$$

The question is now: what is the surface momentum density $\vec{G}^s$? An obvious candidate would be $\bar{g} + \rho^s v^\perp \vec{n}$, where ρ^s and $\bar{g}$ are given by eq.(3.5). But this requires some justification. We will find it in the following general principle. Given a cube C, that is a set of points $\vec{x} = \vec{x}_0 + \sum_{i=1}^{3} \lambda_i \vec{e}_i$ $(\vec{e}_i \cdot \vec{e}_j = \delta_{ij})$ with $\lambda_i \in [0,d]$, let $\Phi_i(\lambda)$ denote the total mass current through the surface $S_{i,\lambda}$ consisting of all points $\vec{x}_0 + \lambda\vec{e}_i + \sum_{j \neq i} \lambda_j \vec{e}_j$, $\lambda_j \in [0,d]$ ($S_{i,0}$ and $S_{i,d}$ are the two faces of the cube perpendicular to $\vec{e}_i$ and $S_{i,\lambda}$ $(0 < \lambda < d)$ is an intermediate "slice" parallel to these two faces). Then the i^{th} component P_i of the total amount of momentum contained in the cube is given by

$$P_i = \int_0^d \Phi_i(\lambda)\, d\lambda \quad .$$

Applying this to a cube C the center of which coincides with a point $\vec{p}$ of Σ_t and no face of which is parallel to $T_{\vec{p}}(\Sigma_t)$, it may be shown, using eq.(2,18), that the i^{th} component of the total momentum contained in C is given by

$$P_i(C) = \int_0^d \Phi_i(\lambda)\, d\lambda = \vec{e}_i \cdot \left[\int_{\Sigma_t(C)} (\bar{g} + \rho^s v^\perp \vec{n})\, dA + \int_C \vec{G}\, dV \right]$$

where $\Sigma_t(C)$ is the patch of Σ_t contained in the cube C. The proof is somewhat technical and will not be reproduced here. Hence the surface momentum density $\vec{G}^S$ is indeed given by

$$\vec{G}^S = \bar{g} + \rho^S v^\perp \vec{n} \quad . \tag{3.9}$$

The surface contribution to the momentum flux follows from eqs.(2.33) and (2.34), putting in the Q field appropriate to linear momentum, which will be denoted by Q_ℓ. The associated M^S and $\bar{\Gamma}$ defined by eq.(2.34) will be denoted by Π^S and $\bar{\Gamma}_\ell$ so that

$$Q_\ell = (\Pi^S)^* + \vec{n} \otimes \bar{\Gamma}_\ell \quad . \tag{3.10}$$

From eq.(2.36) the momentum surface balance equation then reads

$$\frac{d^\perp}{dt}(\bar{g} + \rho^S v^\perp \vec{n}) - 2Hv^\perp(\bar{g} + \rho^S v^\perp \vec{n}) + \mathrm{Div}\Pi^S + \overline{\mathrm{Tr}}(S\Pi^S)\vec{n}$$

$$+ (\mathrm{Div}\bar{\Gamma}_\ell)\vec{n} - S(\bar{\Gamma}_\ell) - \vec{f} + [\![\Pi^*(\vec{n}) - v^\perp \vec{G}]\!] = \vec{0} \tag{3.11}$$

where $\vec{f}$ is the surface momentum source, which may be interpreted as an external surface force per unit area. This equation is hardly suggestive of a surface version of Newton's second law. In that respect the essential element missing is an expression of $\bar{\Gamma}_\ell$ in terms of already defined quantities. The desired expressions will follow from the balance of angular momentum. In the following, given $\vec{A} \in E_3$, we shall denote by $\vec{A}^\times$ the linear operator defined by $\vec{A}^\times(\vec{u}) = \vec{A} \times \vec{u}$. The symbol $\vec{r}^\times$ will stand for a field of linear operators, the one associated to a given point of space $\vec{r}_0$ being $\vec{r}_0^\times$. The bulk density of angular momentum is $\vec{r} \times \vec{G}$ and its surface density will, according to eq.(3.9), be given by

$$\vec{L}^S = \vec{r} \times \vec{G}^S = \vec{r} \times (\bar{g} + \rho^S v^\perp \vec{n}) \quad . \tag{3.12}$$

The flow of angular momentum through the boundary ∂V of a region V fixed in space will be given by

$$\vec{\Phi}_a^* = \int_{\partial V} \vec{r} \times \Pi^*(\vec{N})\, dA + \int_{L_t(\partial V)} [\vec{r} \times Q_\ell(\vec{v}) + \tau v^\perp \vec{L}^s]\, d\lambda \,. \qquad (3.13)$$

It follows that the operator field M of eq.(2.27), which in the case of angular momentum will be denoted by M_a, may be written as

$$M_a = (\vec{r}^{\times} \Pi^*)^* = -\Pi \vec{r}^{\times} \,,$$

since $(\vec{r}^{\times})^* = -\vec{r}^{\times}$. Equation (2.35) then becomes

$$\frac{\partial(\vec{r} \times \vec{G})}{\partial t} - \nabla\cdot(\Pi \vec{r}^{\times}) - \vec{r} \times \vec{F} = \vec{0} \,.$$

In order to evaluate the middle term, we note that if $\vec{e}$ is a constant vector, then

$$\vec{e} \cdot [\nabla\cdot(\Pi \vec{r}^{\times})] = \nabla\cdot[\Pi(\vec{r} \times \vec{e})] = (\nabla\cdot\Pi)\cdot(\vec{r} \times \vec{e}) + \mathrm{Tr}[\Pi\, \nabla(\vec{r} \times \vec{e})]$$
$$= -\vec{e} \cdot (\vec{r} \times \nabla\cdot\Pi) - \mathrm{Tr}(\Pi \vec{e}^{\times}) \,.$$

Now the antisymmetric part of Π may be written as $\vec{\pi}^{\times}$ for a certain vector field $\vec{\pi}$ and the last term above becomes (because of the antisymmetry of $\vec{e}^{\times}$)

$$\mathrm{Tr}(\Pi \vec{e}^{\times}) = \mathrm{Tr}(\vec{\pi}^{\times} \vec{e}^{\times}) = -2\vec{\pi}\cdot\vec{e} \,,$$

and it follows that

$$\nabla \cdot [\Pi \vec{r}^{\times}] = -\vec{r} \times \nabla\cdot\Pi + 2\vec{\pi} \,.$$

Hence the balance equation for angular momentum becomes

$$\frac{\partial(\vec{r} \times \vec{G})}{\partial t} + \vec{r} \times \nabla\cdot\Pi - \vec{r} \times \vec{F} - 2\vec{\pi} = \vec{0}$$

which in view of the balance of momentum (eq.(3.6)), reduces to

$$\vec{\pi} = \vec{0} \,.$$

Thus the antisymmetric part of Π vanishes and

$$\Pi^* = \Pi. \tag{3.14}$$

In the end the bulk angular momentum balance equation is seen to be equivalent to the symmetry of the momentum flux density tensor. This is well-known and simply reflects the absence of local torques due to the absence of a local intrinsic angular momentum density to store up their effects. To derive the consequences of the corresponding *surface* balance equation requires a little more work but is quite straightforward. The final result is expressed in eqs.(3.24) and (3.26) below. First we must find the standard decomposition (eq.(2.34)) of Q_a, the surface Q field pertaining to angular momentum. From eq.(3.13), it follows that

$$Q_a = \vec{r}^{\times}(\Pi^S)^* + \vec{r}^{\times}\vec{n} \circledast \bar{\Gamma}_\ell \quad . \tag{3.15}$$

Accordingly, for any tangent vector $\bar{u}$,

$$\begin{aligned} \vec{n} \cdot Q_a(\bar{u}) &= \vec{n} \cdot \vec{r}^{\times}(\Pi^S)^*(\bar{u}) \\ &= -(\vec{r} \times \vec{n}) \cdot (\Pi^S)^*(\bar{u}) = \Pi^S(\vec{n} \times \vec{r}) \cdot \bar{u} \end{aligned}$$

so that the $\bar{\Gamma}$ surface vector field for angular momentum is

$$\bar{\Gamma}_a = \Pi^S(\vec{n} \times \vec{r}) \quad . \tag{3.16}$$

Likewise from eq.(3.15) it follows that for any tangent vector $\bar{u}$,

$$PQ_a(\bar{u}) = [P\vec{r}^{\times}(\Pi^S)^* + (\vec{r} \times \vec{n}) \circledast \bar{\Gamma}_\ell](\bar{u})$$

which means that M_a^S, the M^S operator for angular momentum, is given by

$$(M_a^S)^* = P\vec{r}^{\times}(\Pi^S)^* + (\vec{r} \times \vec{n}) \circledast \bar{\Gamma}_\ell \quad , \tag{3.17}$$

where use has been made of the general definition of M^S expressed by eq.(2.34) . The above equation is equivalent to

$$M_a^S = -\Pi^S P\vec{r}^{\times} + \bar{\Gamma}_\ell \circledast (\vec{r} \times \vec{n}) \quad . \tag{3.18}$$

In order to write down the surface angular momentum balance equation, we must first evaluate the terms involving M^S and $\overline{\Gamma}$ in eq.(2.36) with the particular M_a^S and $\overline{\Gamma}_a$ given by eqs.(3.16) and (3.18). To evaluate $\mathrm{Div} M_a^S$ at a point $\vec{p}$ of Σ_t, we consider its scalar product with a constant vector $\vec{e} \in T_{\vec{p}}(\Sigma_t)$. If $\bar{e}$ is the surface vector field defined by $\bar{e} = P(\vec{e})$, we know from eq.(1.15) that $\overline{\nabla}\bar{e} = \vec{e}\cdot\vec{n}\, S$, which at $\vec{p}$ reduces to $(\overline{\nabla}\bar{e})_{\vec{p}} = \vec{0}$ since $\vec{e} \in T_{\vec{p}}(\Sigma_t)$. In the calculations that immediately follow, the base point $\vec{p}$, at which $\vec{e}$ is tangent to Σ_t, is omitted but it is understood that all the expressions are evaluated at that point. First we have

$$\begin{aligned}
\bar{e}\cdot \mathrm{Div}[\Pi^S P \vec{r}^{\times}] &= \mathrm{Div}[\Pi^S P \vec{r}^{\times}(\bar{e})] - \overline{\mathrm{Tr}}[\Pi^S P \vec{r}^{\times} \overline{\nabla}\bar{e}] \\
&= \mathrm{Div}[\Pi^S P(\vec{r}\times\vec{e})] \\
&= (\mathrm{Div}\Pi^S)\cdot P(\vec{r}\times\vec{e}) + \overline{\mathrm{Tr}}\{\Pi^S \overline{\nabla}[P(\vec{r}\times\vec{e})]\} \\
&= \bar{e}\cdot P[(\mathrm{Div}\Pi^S)\times\vec{r}] + \overline{\mathrm{Tr}}\{\Pi^S \overline{\nabla}[P(\vec{r}\times\vec{e})]\} .
\end{aligned}$$

But for any tangent vector $\bar{u}$, we have from eqs.(1.4), (1.10), (1.14) and (1.15)

$$\begin{aligned}
\overline{\nabla}_{\bar{u}}[P(\vec{r}\times\vec{e})] &= P D_{\bar{u}}[P(\vec{r}\times\vec{e})] \\
&= P D_{\bar{u}}[\vec{r}\times\vec{e} - \vec{n}\cdot(\vec{r}\times\vec{e})\vec{n}] \\
&= \bar{u}\cdot S(\bar{e})\, P(\vec{r}\times\vec{n}) + \vec{n}\cdot(\vec{r}\times\vec{e})\, S(\bar{u})
\end{aligned}$$

from which

$$\overline{\nabla}[P(\vec{r}\times\vec{e})] = P(\vec{r}\times\vec{n})\otimes S(\bar{e}) + \vec{e}\cdot(\vec{n}\times\vec{r})\, S$$

and

$$\overline{\mathrm{Tr}}\{\Pi^S \overline{\nabla}[P(\vec{r}\times\vec{e})]\} = \bar{e}\cdot[S\Pi^S(\vec{r}\times\vec{n}) + \overline{\mathrm{Tr}}(S\Pi^S)\,\vec{n}\times\vec{r}] .$$

Inserting this in the previous equation for $\mathrm{Div}[\Pi^S P \vec{r}^{\times}]$ we get

$$\mathrm{Div}[\Pi^S P \vec{r}^{\times}] = P[(\mathrm{Div}\Pi^S)\times\vec{r}] + S\Pi^S(\vec{r}\times\vec{n}) + \overline{\mathrm{Tr}}(S\Pi^S)\,\vec{n}\times\vec{r} . \quad (3.19)$$

Next we need the divergence of the last surface tensor in eq.(3.18). On noting that in general

$$\mathrm{Div}\,(\bar{u}\otimes\bar{v}) = (\mathrm{Div}\,\bar{u})\,\bar{v} + (\bar{\nabla}\bar{v})(\bar{u}) \tag{3.20}$$

while

$$\bar{\nabla}(\vec{r}\times\vec{n}) = -\,(\vec{n}^{\times} + P\vec{r}^{\times}S) \tag{3.21}$$

it follows immediately that

$$\mathrm{Div}[\bar{\Gamma}_{\ell}\otimes(\vec{r}\times\vec{n})] = (\mathrm{Div}\,\bar{\Gamma}_{\ell})\,\vec{r}\times\vec{n} - \vec{n}\times\bar{\Gamma}_{\ell} - P[\vec{r}\times S(\bar{\Gamma}_{\ell})]\ .$$

Combining this with eqs.(3.18) and (3.19) gives

$$\mathrm{Div}M_a^S = P\{\vec{r}\times[\mathrm{Div}\,\Pi^S - S(\bar{\Gamma}_{\ell}) + (\mathrm{Div}\,\bar{\Gamma}_{\ell} + \overline{\mathrm{Tr}}(S\Pi^S))\vec{n}]\} + S\Pi^S(\vec{n}\times\vec{r}) - \vec{n}\times\bar{\Gamma}_{\ell}\ . \tag{3.22}$$

From the general relation $\overline{\mathrm{Tr}}(\bar{u}\otimes\bar{v}) = \bar{u}\cdot\bar{v}$ and eq.(3.18) we then get

$$\overline{\mathrm{Tr}}(SM^S) = -\,\overline{\mathrm{Tr}}(S\Pi^S P\vec{r}^{\times}) + S(\bar{\Gamma}_{\ell})\cdot(\vec{r}\times\vec{n}) \tag{3.23}$$

while using eqs.(3.16) and (3.21)

$$\mathrm{Div}\,\bar{\Gamma}_a = \mathrm{Div}[\Pi^S(\vec{n}\times\vec{r})]$$
$$= \vec{n}\cdot[\vec{r}\times\mathrm{Div}\,\Pi^S] + \overline{\mathrm{Tr}}(S\Pi^S P\vec{r}^{\times}) + \overline{\mathrm{Tr}}(\Pi^S\vec{n}^{\times})\ .$$

Combining this with eqs.(3.22) and (3.23) we finally get

$$\mathrm{Div}M_a^S + \overline{\mathrm{Tr}}(SM_a^S)\,\vec{n} + (\mathrm{Div}\,\bar{\Gamma}_a)\,\vec{n} - S(\bar{\Gamma}_a) =$$
$$\vec{r}\times\{\mathrm{Div}\,\Pi^S - S(\bar{\Gamma}_{\ell}) + [\mathrm{Div}\,\bar{\Gamma}_{\ell} + \overline{\mathrm{Tr}}(S\Pi^S)]\vec{n}\} - \vec{n}\times\bar{\Gamma}_{\ell} + \overline{\mathrm{Tr}}(\Pi^S\vec{n}^{\times})\,\vec{n}\ .$$

For briefness let us denote this expression by $\vec{\Omega}$. With the surface source term $\vec{r}\times\vec{f}$ (see eq.(3.11)), the surface balance equation for angular momentum, according to eq.(2.36), will read

$$\frac{d^{\perp}}{dt}[\vec{r}\times(\bar{g} + \rho^S v^{\perp}\vec{n})] - 2Hv^{\perp}[\vec{r}\times(\bar{g} + \rho^S v^{\perp}\vec{n})] + \vec{\Omega}$$
$$- \vec{r}\times\vec{f} + \mathrm{II}\,\vec{r}^{\times}\Pi^*(\vec{n}) - v^{\perp}\vec{r}\times\vec{G}\,\mathrm{II} = \vec{0}\ .$$

However, when it is noted that $\frac{d^{\perp}\vec{r}}{dt} = v^{\perp}\vec{n}$ and use is made of eq.

(3.11), this complicated equation reduces to

$$\vec{n} \times (v^{\perp}\bar{g} - \bar{\Gamma}_{\ell}) + \overline{Tr}(\Pi^{S}\vec{n}^{\times})\,\vec{n} = \vec{0}$$

which is equivalent to

$$\bar{\Gamma}_{\ell} = v^{\perp}\bar{g} \tag{3.24}$$

and

$$\overline{Tr}(\Pi^{S}\vec{n}^{\times}) = 0 \ . \tag{3.25}$$

Now, any antisymmetric linear operator on $T_{\vec{p}}(\Sigma_t)$ may be written as $\alpha\vec{n}^{\times}$ for some number α so that, denoting by Π_0^S the symmetric part of Π^S and by $\alpha\vec{n}^{\times}$ its antisymmetric part, eq.(3.25) becomes

$$0 = \overline{Tr}[(\Pi_0^S + \alpha\vec{n}^{\times})\,\vec{n}^{\times}]$$

$$= \alpha\overline{Tr}[\vec{n}^{\times}\vec{n}^{\times}] = \alpha\overline{Tr}(-I) = -2\alpha$$

so that

$$(\Pi^S)^* = \Pi^S \ . \tag{3.26}$$

Thus the surface angular momentum balance equation, when combined with the surface momentum balance equation, is equivalent to the pair of equations (3.24) and (3.26). These equations imply that the Q field associated to linear momentum may be rewritten as

$$Q_{\ell} = \Pi^S + v^{\perp}\vec{n} \otimes \bar{g} \ .$$

We now *define* a surface tangential velocity field $\bar{v}$ in terms of ρ^S and $\bar{g}$ by writing

$$\bar{g} \equiv \rho^S \bar{v} \ . \tag{3.27}$$

The above equation then becomes

$$Q_{\ell} = \Pi^S + \rho^S v^{\perp}\vec{n} \otimes \bar{v} \ . \tag{3.28}$$

Whereas the surface quantities ρ^S and $\bar{g}$ may be considered to have operational definitions contained in eqs.(2.19) and (2.21)

with $a^s = \rho^s$ and $\bar{j} = \bar{g}$, the tangential velocity $\bar{v}$ has no independent operational definition within the present "minimal" framework. It is first introduced in eq.(3.27), as a *derived* quantity. In an intuitive "material" picture of the dividing surface, this equation would seem physically obvious and we would tend to consider $\bar{v}$ as a "primitive observable". We will now see that the surface momentum balance equation derived in the minimal theory may be cast in just the same form as one would expect on the basis of such intuitive interpretations of the dividing surface and of $\bar{v}$. To this,end a non-tangential velocity distribution $\vec{V}$ is defined on Σ_t by

$$\vec{V} = \bar{v} + v^\perp \vec{n} \tag{3.29}$$

where $v^\perp$ is the normal velocity of Σ_t and $\bar{v}$ is defined by eq.(3.27). When this is inserted in eq.(3.11) and use is made of eq.(3.4) to move ρ^s to the left of the time derivative, the following equation is obtained

$$\rho^s \Big[\frac{d^\perp \bar{v}}{dt} + \bar{\nabla}_{\bar{v}} \bar{v} + \bar{v}\cdot S(\bar{v})\,\vec{n} + \Big(\frac{d^\perp v^\perp}{dt} + \bar{v}\cdot \mathrm{Grad}\, v^\perp\Big)\vec{n} - v^\perp(\mathrm{Grad}\, v^\perp + S(\bar{v}))\Big]$$
$$+ \mathrm{Div}(\Pi^s - \rho^s \bar{v}\otimes\bar{v}) + \overline{\mathrm{Tr}}[S(\Pi^s - \rho^s \bar{v}\otimes\bar{v})]\,\vec{n} - \vec{f}$$
$$+ [\![\Pi(\vec{n}) - v^\perp \vec{G} - (\vec{G}\cdot\vec{n} - \rho v^\perp)\vec{V}]\!] = \vec{0}\,.$$

Let us denote by $\frac{D}{Dt}$ the time derivative along the trajectory $\vec{Q}(t)$ defined by $\vec{Q}(t) \in \Sigma_t$ and $\dot{\vec{Q}}(t) = \vec{V}(\vec{Q}(t))$ for each t, where $\vec{V}$ is defined by eq.(3.29). It follows from eqs.(1.19),(1.20) and (1.27) that the complicated expression multiplying ρ^s in the above equation is simply equal to $\frac{D}{Dt}\vec{V}$. Introducing a surface stress tensor

$$T^S \equiv -(\Pi^S - \rho^S \bar{v} \otimes \bar{v}) \tag{3.30}$$

the momentum balance equation becomes

$$\rho^S \frac{D\vec{V}}{Dt} = \mathrm{Div} T^S + \overline{\mathrm{Tr}}(ST^S)\vec{n} + \vec{f} + [\![[T - \rho(\vec{V} - \vec{w}) \otimes (\vec{V} - \vec{w})](\vec{n})]\!] . \tag{3.31}$$

We may if we wish give a very intuitive interpretation of this equation. The term on the left may be viewed as mass (per unit area) times acceleration. By analogy with bulk continua, the surface stress tensor can be imagined as representing internal surface forces according to the prescription that the total force $\vec{F}$ acting on a patch of surface $S \subset \Sigma_t$ bounded by the closed curve ∂S, due to the the surrounding "interfacial matter" is given by

$$\vec{F} = \int_{\partial S} (T^S)^*(\bar{\nu})\, d\lambda . \tag{3.32}$$

This integral is easily transformed into

$$\vec{F} = \int_S [\mathrm{Div} T^S + \overline{\mathrm{Tr}}(ST^S)\vec{n}]\, dA \tag{3.33}$$

showing that the first two terms on the right-hand side of eq.(3.31) may be interpreted as the resultant per unit area of local surface contact forces. The term $\vec{f}$ may be viewed as external surface force per unit area, and the last term as arising form the interaction between the interface and the adjoining phases. This informal picture is quite satisfying intuitively. It is good to know that it may be developed from the minimal assumptions introduced in Sections 2 and 3, which are themselves independent of such intuitive representations. The crucial step in deducing the intuitively appealing eq.(3.31) form the abstract eq.(3.11) was the obtention of eq.(3.24),

via the balance of angular momentum.

At equilibrium, T^S reduces to γI, where γ is the surface or interfacial tension (Aveyard and Vincent [1977]), and from the general identity $\mathrm{Div}(\alpha A) = A^*(\mathrm{Grad}\,\alpha) + \alpha\,\mathrm{Div}\,A$ valid for any scalar and linear operator fields α and A on Σ, we get

$$\mathrm{Div}\,T^S = \mathrm{Div}\,\gamma I = \mathrm{Grad}\,\gamma \ .$$

On the other hand, it follows from eq.(II.1.13) that $\overline{\mathrm{Tr}}(ST^S) = \overline{\mathrm{Tr}}(S\gamma I) = 2\gamma H$, while $T = -pU$ (U is the identity on E_3), so that eq.(3.31) reduces to

$$\mathrm{Grad}\,\gamma + 2\gamma H\vec{n} + \vec{f} - (p^+ - p^-)\vec{n} = \vec{0}$$

whose tangential and normal projections are

$$\mathrm{Grad}\,\gamma + \bar{f} = \vec{0}$$

and

$$p^+ - p^- = f^\perp + 2\gamma H \ .$$

The second of these relations is the well known Laplace equation, which implies that the pressure inside a liquid drop is higher than that of the surrounding vapor.

The balance of linear momentum at the empirical level has naturally been considered by all authors who worked in this field. We may quote in particular Scriven [1960], Slattery [1964], Ghez [1966], Moeckel [1975], Murdoch [1976], Bedeaux, Albano and Mazur [1975], Kovac [1976] and Vodák [1978 a,b]. The derivation given in this section distinguishes itself by the minimal amount of assumptions made about the dividing surface. Thus no appeal was made to intuitive notions of surface material velocity or of surface contact forces. As a result, the formalism, which is incidentally com-

patible with a "material" conception of the dividing surface, is also fully compatible with the Gibbs approach, though neither points of view were relied upon in the derivation. This confers a high degree of generality to the equations. To stress this point we note that, if the Gibbs approach were adopted, the surface excess mass density ρ^s would be interpreted as an adsorption (in mass units) and as such, with certain choices of the dividing surface , it could very well be *negative*. Yet our momentum balance equations would hold true just as well. The price paid for this generality is the slightly increased complexity of the derivation.

The surface balance of angular momentum as given for instance by Scriven [1960] and Slattery [1964] and other authors quoted above is used only to establish the symmetry of the surface stress tensor. In the new formulation given here, it serves the additional purpose of bringing the very general but abstract momentum balance equation (eq.(3.11)) into the more familiar form expressed in eq. (3.31). We consider it of some interest that this intuitive form can be arrived at on the sole basis of a postulated Q field for the surface flow of momentum (which is the very least that one can assume), and the surface balance of angular momentum.

4) Energy

Our aim in this chapter has been to give an account of the empirical approach to interfacial dynamics that will serve as a basis for comparison with the more fundamental theory developed

in subsequent chapters. In order to get as clear as possible a picture of what can be said at a strictly empirical level, we have strived to minimize the number of assumptions and to justify all results not by intuitive arguments but by deductions from general principles. All our assumptions are contained in eqs.(2.5-2.9). So the consequences derived so far must hold in any theory that contains these assumptions, irrespective of the specific interpretation it makes of the surface Σ or of the surface fields defined on it in terms of the diffuse structure of the transition zone. A good example of this is the way we arrived at eq.(3.9) for the momentum surface excess density, or at eq.(3.31). Using eqs.(3.27) and (3.29), eq. (3.9) may be rewritten as

$$\vec{G}^s = \rho^s \vec{V} . \tag{4.1}$$

Although a priori evident, or so it seems (note that in the Gibbs approach, ρ^s could be negative), we nevertheless showed how this result could be derived from a general principle relating momentum flux and momentum density (see the argument preceding eq.(3.9)).

Coming now to the kinetic energy surface excess, nothing could seem more natural than setting it equal to $\frac{1}{2}\rho^s V^2$. At the empirical level, one would indeed be hard pressed to suggest anything else. To make the point as clear as possible, the question is this: Under the assumption that the total mass $M(V)$ and the total momentum $\vec{P}(V)$ in any region V are given by

$$M(V) = \int_V \rho \, dV + \int_{\Sigma_t(V)} \rho^s \, dA$$

and

$$\vec{P}(V) = \int_V \rho \vec{w}\, dV + \int_{\Sigma_t(V)} \rho^s \vec{V}\, dA ,$$

can we argue from some general principle that the total macroscopic kinetic energy (neglecting diffusion kinetic energy if present) in V, $K(V)$, is given by

$$K(V) = \int_V \tfrac{1}{2}\rho w^2\, dV + \int_{\Sigma_t(V)} \tfrac{1}{2}\rho^s V^2\, dA \quad ? \tag{4.2}$$

Surprisingly the answer is no. This simply cannot be proved and must be considered as an additional assumption. As we shall see in Chapter V, when mass and momentum densities are considered more fundamentally as continuously varying field in the transition zone, and surface excess densities are given explicit definitions in a generalized Gibbs approach, the above expression for the kinetic energy surface excess is found to hold only when certain residual terms can be neglected, even in a context where eqs.(2.19-24) are fully justified. In contrast to this, the general theory will confirm that eq.(4.2) holds true in such a context. This possible complication with the kinetic energy is just a particular instance of a general situation: when we construct some bulk density a by a nonlinear expression $a = f(a_1,\ldots,a_n)$ involving other bulk densities $a_1,\ldots,a_n$, it cannot be said that the surface excess density a^s associated to a is necessarily equal to the same expression wherein the bulk densities $a_1,\ldots,a_n$ are replaced by their associated surface excess densities $a_1^s,\ldots,a_n^s$. (In the case of kinetic energy, the bulk densities involved are mass and momentum densities ρ and $\vec{G}$ and

the nonlinear expression is $\rho^{-1}\vec{G}\cdot\vec{G}$). This complication, to which we shall return in Chapter V, does not seem to have been explicitly recognized in the literature.

The balance equation for $\rho^s \frac{V^2}{2}$ follows naturally from the momentum balance equation. From the definition of the $\frac{D}{Dt}$ time derivative given after eq.(3.29) and from eq.(1.19), it follows that

$$\frac{D\rho^s}{Dt} = \frac{d^\perp \rho^s}{dt} + \bar{v} \cdot \mathrm{Grad}\,\rho^s$$

which, combined with eq.(3.4), gives

$$\rho^s \frac{D}{Dt}\left(\frac{V^2}{2}\right) = \frac{D}{Dt}\left(\rho^s \frac{V^2}{2}\right) - 2Hv^\perp \rho^s \frac{V^2}{2} + \frac{V^2}{2}\rho^s \mathrm{Div}\,\bar{v} + \frac{V^2}{2}[\![\vec{G}\cdot\vec{n} - \rho v^\perp]\!] .$$

Taking the dot product of eq.(3.31) with $\vec{V}$ and replacing the left-hand side by the above expression for $\rho^s \frac{D}{Dt}\left(\frac{V^2}{2}\right)$ yields the desired result:

$$\frac{d^\perp}{dt}\left(\rho^s \frac{V^2}{2}\right) - 2Hv^\perp \rho^s \frac{V^2}{2} + \mathrm{Div}\left[\rho^s \frac{V^2}{2}\bar{v} - T^s(\bar{v})\right] + \overline{\mathrm{Tr}}\left[T^s(\bar{\nabla}\bar{v} - v^\perp S)\right]$$

$$- \vec{f}\cdot\vec{V} + [\![-\vec{V}\cdot T(\vec{n}) + (\vec{G}\cdot\vec{n} - \rho v^\perp)(\vec{V}\cdot\vec{w} - \frac{V^2}{2})]\!] = 0 . \qquad (4.3)$$

Comparing this result with eq.(2.24) enables us to identify the surface current density and source term associated with $\rho^s \frac{V^2}{2}$ as $\rho^s \frac{V^2}{2}\bar{v} - T^s(\bar{v})$ and $-\overline{\mathrm{Tr}}\left[T^s(\bar{\nabla}\bar{v} - v^\perp S)\right] + \vec{f}\cdot\vec{V}$. There is no question that eq.(4.3) is the correct balance equation for the quantity $\rho^s \frac{V^2}{2}$. But if this quantity is indeed the kinetic energy surface excess, its balance equation must also follow from the general

surface balance equation (2.24), feeding in the appropriate bulk kinetic energy terms for the jump $[\![\vec{J}\cdot\vec{n} - av^{\perp}]\!]$. The bulk current density $\vec{J}$ associated to kinetic energy is $\frac{\rho w^2}{2}\vec{w} - T(\vec{w})$ while $av^{\perp}$ becomes $\frac{\rho w^2}{2}v^{\perp}$. From the above identification of surface current density and surface source term for $\rho^S\frac{V^2}{2}$, there follows an alternative surface balance equation for $\rho^S\frac{V^2}{2}$:

$$\frac{d^{\perp}}{dt}(\rho^S\frac{V^2}{2}) - 2Hv^{\perp}\rho^S\frac{V^2}{2} + \mathrm{Div}\,[\rho^S\frac{V^2}{2}\bar{v} - T^S(\bar{v})] + \overline{\mathrm{Tr}}\,[T^S(\bar{\nabla}\bar{v} - v^{\perp}S)]$$

$$- \vec{f}\cdot\vec{V} + [\![[\frac{\rho w^2}{2}\vec{w} - T(\vec{w})]\cdot\vec{n} - \frac{\rho w^2}{2}v^{\perp}]\!] = 0 . \qquad (4.4)$$

It is compatible with eq.(4.3) only if

$$[\![-\vec{V}\cdot T(\vec{n}) + (\vec{G}\cdot\vec{n} - \rho v^{\perp})(\vec{V}\cdot\vec{w} - \frac{V^2}{2})I]\!] = [\![[\frac{\rho w^2}{2}\vec{w} - T(\vec{w})]\cdot\vec{n} - \frac{\rho w^2}{2}v^{\perp}]\!] ,$$

which may be cast into the simpler form

$$\vec{n}\cdot[\![(T - \frac{\rho w_{\mathcal{R}}^2}{2}U)(\vec{w}_{\mathcal{R}})]\!] = 0 \qquad (4.5)$$

where

$$\vec{w}_{\mathcal{R}} \equiv \vec{w} - \vec{V} \qquad (4.6)$$

and U is the identity operator on E_3. This conclusion seems inescapable inasmuch as we accept first $\rho^S\frac{V^2}{2}$ as the correct expression for the kinetic energy surface excess and secondly the surface current density and source terms $\rho^S\frac{V^2}{2}\bar{v} - T^S(\bar{v})$ and $-\overline{\mathrm{Tr}}\,[T^S(\bar{\nabla}v - v^{\perp}S)] + \vec{f}\cdot\vec{V}$ as those appropriate for the kinetic energy. By virtue of the generality of our formulation, it follows that this state of affairs obtains no matter what specific inter-

pretation is given to the dividing surface and to the surface fields. But it has been overlooked in all the studies that we know of where the surface balance of kinetic energy was considered.

Equation (4.5) is satisfied if $\vec{w}^+ \cdot \vec{n} = \vec{w}^- \cdot \vec{n} = v^\perp$ on Σ_t and either $\vec{n}$ or both $\vec{w}^+_\pi$ and $\vec{w}^-_\pi$ are eigenvectors of T^+ and T^- on Σ_t. This is a sufficient but of course not necessary condition. Another sufficient but not necessary condition is that $\vec{w}^+ = \vec{w}^- = \vec{V}$ on Σ_t. We shall get better insight into this matter when we consider it again in Chapter V from the point of view of the general theory developed in the next two chapters.

The balance of kinetic energy is of course an intermediate step towards the balance of internal energy which in turn leads to the balance of entropy and to the expression for the entropy production, which is the starting point for the derivation of linear constitutive relations in phenomenological non-equilibrium thermodynamics. Since the results thereby obtained are rather involved, and since we shall not need them in subsequent developments, the reader is refered to the literature quoted in Section 2 of Chapter I, particularly to the works of Bedeaux et al [1975], Kovac [1978] and Vodák [1978 b].

In bulk phases, the balance equation for combined kinetic and internal energy $e = u + \frac{1}{2}\rho w^2$, ignoring external fields for simplicity, is

$$\frac{\partial e}{\partial t} + \nabla \cdot (e\vec{w} - T(\vec{w}) + \vec{J}_q) = 0 \,. \tag{4.7}$$

On substracting from this the balance equation for kinetic energy

$$\frac{\partial}{\partial t}\left(\rho\frac{w^2}{2}\right) + \nabla\cdot\left(\rho\frac{w^2}{2}\vec{w} - T(\vec{w})\right) + \mathrm{Tr}(T\nabla\vec{w}) = 0 \ ,$$

there follows the balance equation for internal energy

$$\frac{\partial u}{\partial t} + \nabla\cdot(u\vec{w} + \vec{J}_q) - \mathrm{Tr}(T\nabla\vec{w}) = 0 \ . \tag{4.8}$$

In writing down the corresponding surface balance equations, all authors proceed by analogy. In our notations, this means that the balance equations for the energy surface excess is written as

$$\frac{d^{\perp}e^S}{dt} - 2Hv^{\perp}e^S \quad \mathrm{Div}[e^S\bar{v} - T^S(\bar{v}) + \bar{J}_q \,] \tag{4.9}$$

$$+ [\![(e\vec{w} - T(\vec{w}) + \vec{J}_q)\cdot\vec{n} - ev^{\perp}]\!] = 0$$

which, combined with eq. (4.3), yields the following surface balance equation for internal energy:

$$\frac{d^{\perp}u^S}{dt} - 2Hv^{\perp}u^S + \mathrm{Div}(u^S\bar{v} + \bar{J}_q) - \overline{\mathrm{Tr}}[T^S(\bar{\nabla}\bar{v} - v^{\perp}S)] \tag{4.10}$$

$$+ [\![\vec{n}\cdot[(u + \tfrac{1}{2}\rho w_{\ell}^2)\vec{w}_{\ell} - T(\vec{w}_{\ell}) + \vec{J}_q]]\!] = 0 \ .$$

Now it should be stressed that eq.(4.9) is obtained on the basis of analogy and analogy *alone*. Once we have identified e^S as the surface energy excess and $\bar{J}_q$ as the surface excess heat current density, there is in principle no freedom left in the choice of the surface excess energy current density. That it may be written as $e^S\bar{v} - T^S(\bar{v}) + \bar{J}_q$ is an additional *assumption*. We emphasize that contrary to eq.(4.1), we have not deduced this expression from a general principle. If the surface Σ were a model of a free liquid film, we could in fact justify this choice on the basis of a work principle. But in the present case we, at least, cannot think of any way of doing this.

CHAPTER III

THE DEVIATION APPROACH

1) Towards a more general theory

In the previous chapter, we have aimed at presenting the phenomenological approach by starting with a set of minimal assumptions and trying to develop the rest either as direct consequences of these assumptions or of these assumptions coupled with well-established general principles. This proved possible except for the energy-related equations which required additional special assumptions whose sole basis was their plausibility. The approach followed throughout Chapter II was fully phenomenological in the sense that no reference whatsoever was made about the interpretation of the surface fields in terms of the microscopic diffuse structure of the interface.

In Chapter I, we saw that the Gibbs approach provided a beautifully simple and yet exact rational basis for explicitely interpreting the equilibrium surface excess densities. In view of its attractiveness, it is worth studying the possible extension of this method into the realm of non-equilibrium. It is to this matter that the rest of this work is devoted, while the first part will provide us with a background against which the forthcoming results may be conveniently compared. We shall now describe in broad terms what these results are all about.

The object of our considerations is a non-equilibrium n-component two-phase fluid system. We now explicitely recognize the three-dimensional character of the transition zone, and let the system be described by densities, current densities and source densities, typical ones being denoted by a^*, $\vec{J}^*$ and σ^*, that vary continously across the interface. With the help of these densities one may compute the total amount $A^*(V)$ of attribute a^* in a region fixed in space V, its flow through ∂V, $\Phi^*(\partial V)$, and its rate of production in V, $P^*(V)$. These quantities obey the balance equation

$$\frac{d}{dt} A^*(V) + \Phi^*(\partial V) - P^*(V) = 0 \ . \qquad (1.1)$$

As in equilibrium, the first step consists in introducing a dividing surface located somewhere in the transition zone, and in extrapolating the bulk densities in both phases up to this dividing surface. This means that they are subject to the usual balance equations and that they obey the bulk constitutive relations right up to the dividing surface. We call these densities, which in general differ from the exact densities in the transition zone and may present jump discontinuities at the dividing surface, the schematic densities. The fields equal to the difference between exact and bulk densities, we call deviations. They vanish outside the transition zone.

We next come to the second step which involves two parts. The first is to introduce surface excess quantities that will compensate for the errors following the use of schematic densities in computing the total amount of an attribute in a region V encompass-

ing part of the dividing surface. The exact relations obtained in this context differ from those used in the empirical approach but complete agreement obtains in a certain well defined zeroth order approximation. The second part concerns the dynamics. Equation (1.1) is satisfied for any region V not intersecting the transition zone provided that the bulk densities obey the usual differential balance equations. In the transition zone, the exact densities are the sum of the schematic densities and of the deviations. We will obtain a necessary and sufficient condition in order that eq.(1.1) shall also hold for any region V containing part of the dividing surface. This exact relation involving the bulk field jumps and appropriate surface moments of the deviations is *formally* identical with the surface balance equation used in the empirical approach. We shall explain why this formal identity is remarkable and see how the differences that remain in the detailed interpretation of the surface fields disappear in a suitable zeroth order approximation.

A basic premise of our theory is that the detailed structure of the transition zone may be described by exact densities a^*, $\vec{J}^*$ and σ^* obeying the relation

$$\frac{\partial a^*}{\partial t} + \nabla\cdot\vec{J}^* - \sigma^* = 0 \qquad (1.2)$$

everywhere including inside the interface. This type of relation is one basic ingredient in the phenomenological treatment of bulk fluids. As is well-known (Kreuzer and Beamish [1977]), such relations may be derived from microscopic theory using reduced distri-

bution functions and the first equation of the BBGKY hierarchy. In the present context, the status of eq.(1.2) is somewhat different. For the phenomenological approach to interfacial dynamics makes no use of exact densities and consequently of eq.(1.2) in the transition zone. It rather *postulates* surface excess densities and derives a *surface* balance equation (eq.(II.2.24)). So our justification for using eq.(1.2) in the interface rests directly on the microscopic theory. Specifically, what we assume is that the microscopic theory of reduced distribution functions can provide (probalistic) expressions for mass, momentum and energy densities and current densities, valid in the transition zone, and satisfying balance equations like eq.(1.2). The use of reduced distribution functions in the interface is in fact common practice in the statistical mechanics of the equilibrium interface (Navascues [1979]), and there is no need here to go through an explicit microscopic derivation of the balance equations, because the calculations are essentially the same as for bulk phases. The only difference is that linearization of the pair distribution dependence on the center of mass of two molecules (Green [1969],p.36) cannot be made in the transition zone. But that does not prevent one from arriving at the balance equations (see for instance Gray [1968],p.514-520). In a paper mainly devoted to equilibrium questions, Carey, Scriven and Davis [1978] have given such a derivation for the case of momentum.

2) Density integrals, currents and surface normal moments

In this section, we give the explicit construction of the surface quantities in terms of which the theory is formulated. We introduce "surface normal moments" as convenient building blocks. These are used to define surface excess densities which are the exact analogues of the "adsorptions" defined in the equilibrium Gibbs approach (Defay et al: [1966]), and surface current densities which are not present in the equilibrium theory. The rigourous expressions for the total amount of an attribute in a region V or its flow through the boundary ∂V are not identical with those found in the empirical approach (eqs.(2.19)and (2.21)), but complete agreement is obtained in a suitable zeroth order approximation that will be discussed later. However, as we shall see in section 3, a rigorous surface balance equation is arrived at which is *formally* undistinguishable from that obtained in the empirical approach. This is quite remarkable.

Many notations are carried over from Section 2 of Chapter II. The dividing surface at time t is denoted by Σ_t, its unit normal by $\vec{n}$ and the regions M_t^+ and M_t^- have the same definitions as in the previous context. The densities a, σ and $\vec{J}$, defined everywhere in the material in terms of the extrapolated bulk densities by $a(\vec{r}) = a^+(\vec{r})$ if $\vec{r} \in M_t^+$ and $a(\vec{r}) = a^-(\vec{r})$ if $\vec{r} \in M_t^- - \Sigma_t$ (with similar definitions for σ and $\vec{J}$), will be called *schematic densities*. Their jumps at the dividing surface are again defined by eq.(II.2.4). The name *deviation* will be given to the functions

defined everywhere in the material by

$$a' = a^* - a \quad , \quad \sigma' = \sigma^* - \sigma \quad \text{and} \quad \vec{J}' = \vec{J}^* - \vec{J} \quad . \tag{2.1}$$

It follows from the definitions that

$$\frac{\partial a^*}{\partial t} + \nabla \cdot \vec{J}^* - \sigma^* = 0 \tag{2.2}$$

everywhere in the material, while

$$\frac{\partial a}{\partial t} + \nabla \cdot \vec{J} - \sigma = 0 \quad \text{and} \quad \frac{\partial a'}{\partial t} + \nabla \cdot \vec{J}' - \sigma' = 0 \tag{2.3}$$

in the interior of M_t^+ and of M_t^- . The same comments that were made after eq.(II.2.10) about the meaning of derivatives still hold.

A convenient and physically reasonable hypothesis about the deviations a',σ' and $\vec{J}'$ is that they vanish everywhere except in a very thin layer enveloping the dividing surface. Strictly speaking this hypothesis might not be verified in an exact solution. For instance, if for some $\vec{p} \in \Sigma_t$, the function $\zeta \to a'(\vec{p}+\zeta\vec{n}(\vec{p}))$ happened to be analytic on the interval $(0,\infty)$, it could not vanish on some subinterval (ζ_0,∞) without vanishing on $(0,\zeta_0]$ as well. Granted that such a possibility definitely exists, it is nevertheless certainly still safe to assume on physical grounds that, for ζ outside some very short interval $(-\delta,\delta)$, $a'(\vec{p}+\zeta\vec{n}(\vec{p}))$ is completely negligible. Should that not be the case, this whole scheme would be of no interest in the first place! For the sake of technical simplicity then, the convenient hypothesis of strict vanishing of the deviations at a very short distance from the dividing surface will be retained.

Given a surface Σ with unit normal vector $\vec{n}$, and a num-

ber ζ, the surface parallel to Σ at distance ζ, Σ^{ζ} , is by definition the set of points $\vec{p}+\zeta\vec{n}(\vec{p})$, where $\vec{p}$ ranges over Σ (O'Neill [1970]). The above hypothesis on the deviations may be reformulated thus: it is assumed that there exists a small distance δ such that outside the transition region I_t (I for interface) sandwiched between the surfaces $\Sigma_t^{-\delta}$ and Σ_t^{δ} parallel to Σ_t, the three deviations a', σ' and $\vec{J}'$ vanish. The same value of δ may be assumed to work throughout any time interval of interest.

Naturally the dividing surface is chosen so that it bends sensibly only on a macroscopic scale, that is the normal curvature $\kappa_{\vec{p}}(\hat{u})$ in any direction $\hat{u}$ (see eq.(II.1.12)) is negligible compared to $1/\delta$. Its location is further restricted by the requirement that the variations of the exact densities along the dividing surface must be small compared to those along the normal: variations along the dividing surface are on a spatially slow, that is macroscopic, scale. This is tantamount to the requirement that the direction of $\vec{n}(\vec{p})$ be close to those of the gradients of the exact densities at $\vec{p}$.

The following symbols for density integrals will be adopted:

$$A(V) \equiv \int_V a \, dV \ , \ A^*(V) \equiv \int_V a^* \, dV \ , \ A'(V) \equiv \int_V a' \, dV \qquad (2.4)$$

with similar obvious definitions for the integrals of the source terms $P(V)$, $P^*(V)$ and $P'(V)$. Likewise we shall write

$$\Phi(\partial V) \equiv \int_{\partial V} \vec{J}\cdot\vec{N} \, dA \ , \ \Phi^*(\partial V) \equiv \int_{\partial V} \vec{J}^*\cdot\vec{N} \, dA \ , \ \Phi'(\partial V) \equiv \int_{\partial V} \vec{J}'\cdot\vec{N} \, dA \ . \qquad (2.5)$$

To avoid repeated circumlocutions, we shall further agree

on a set of notations used throughout the rest of this work. Some of the objects defined are already illustrated in Fig.1 of Section 2 of Chapter II, while the others are illustrated in Fig.2 . Consider a *fixed* region V intersecting Σ_t and extending beyond the transition region I_t (defined above), into M_t^+ and M_t^- . The outward unit normal to ∂V is denoted by $\vec{N}$; the patch of Σ_t contained in V, by $\Sigma_t(V)$; the boundary $\partial[\Sigma_t(V)]$ of this patch, which may be described as the curve along which ∂V meets with Σ_t, by $L_t(\partial V)$; and the strip of the surface ∂V lying between the parallel surfaces $\Sigma_t^{-\delta}$ and Σ_t^{δ}, by $\Delta_t(\partial V)$. The "belt" consisting of all points $\vec{p}+\zeta\vec{n}(\vec{p})$ with $\vec{p} \in L_t(\partial V)$ and $\zeta \in [-\delta,\delta]$, is denoted by $\beta_t^{\perp}(\partial V)$, and the part of I_t circumscribed by and includind this belt, by $I_t(V)$. The unit normal to $\beta_t^{\perp}(\partial V)$, pointing away from $I_t(V)$, is denoted by $\vec{N}^*$. The region bounded on top and bottom by Σ_t^{δ} and $\Sigma_t^{-\delta}$, and on the sides by $\Delta_t(\partial V)$ and $\beta_t^{\perp}(\partial V)$, is denoted by $X_t(\partial V)$; its cross-section looks like the union of the top and bottom surfaces comprised between the bars of the letter X. A function Θ is defined, first in the interior of $X_t(\partial V)$, by $\Theta(\vec{r}) = -1$ if $\vec{r}$ is inside $I_t(V)$, and $\Theta(\vec{r}) = 1$ if $\vec{r}$ is outside $I_t(V)$; it is then extended to the boundary of $X_t(\partial V)$, deprived of $L_t(\partial V)$, by continuity. (The function Θ usually has a jump when $\vec{r}$ goes from the + to the - part of $X_t(\partial V)$.) The outward unit normal to the curve $L_t(\partial V)$ is denoted by $\bar{\nu}$; this vector is tangent to Σ_t. The direction of $\bar{T}$, unit tangent vector to $L_t(\partial V)$ is chosen so that $\bar{\nu}\times\bar{T} = \vec{n}$. Since the curve $L_t(\partial V)$ lies in ∂V, it follows that $\vec{N}$ is perpendicular to $\bar{T}$, so that $\vec{N}$ lies in the plane spanned by $\vec{n}$ and $\bar{\nu}$.

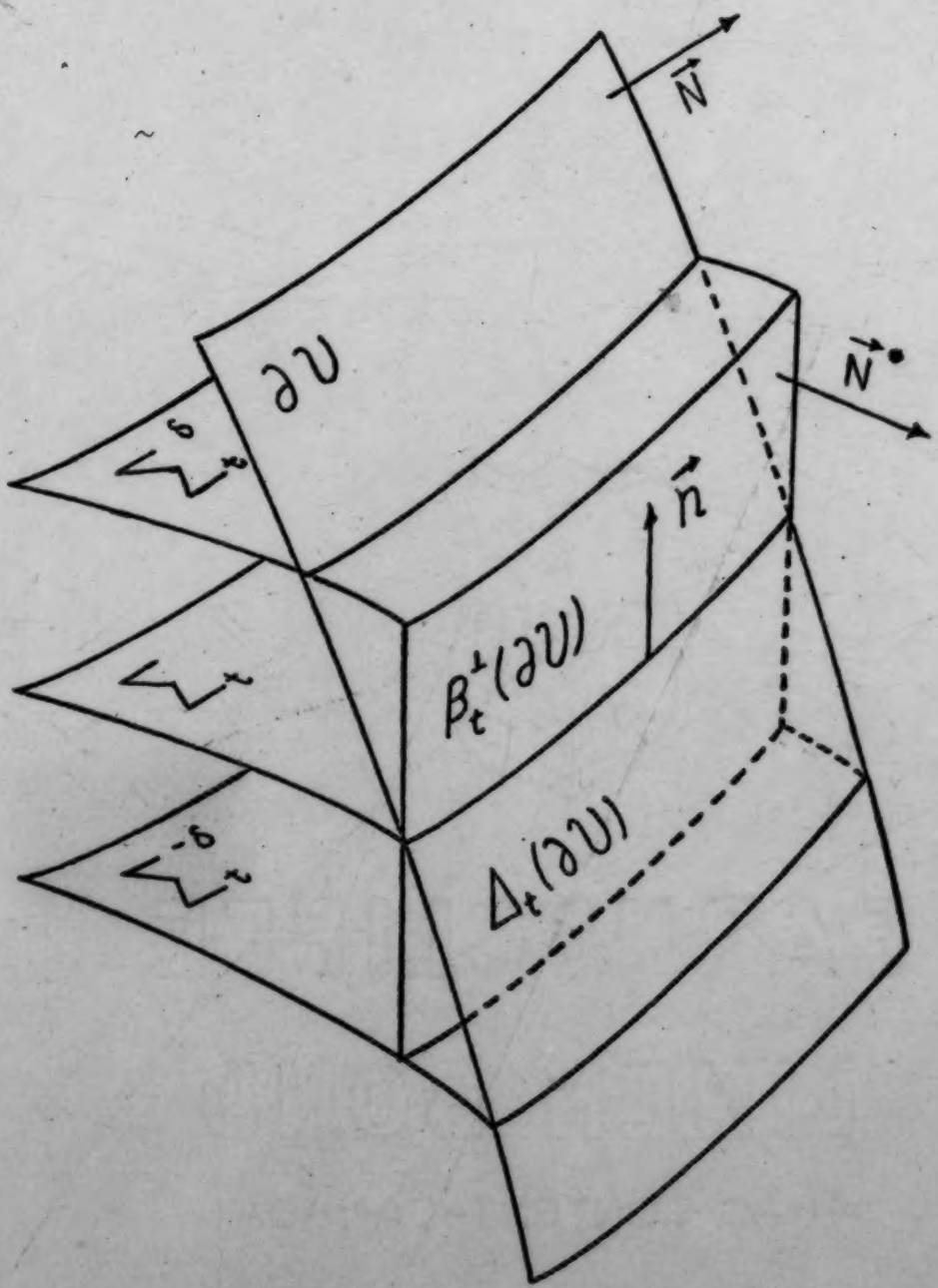

Figure 2: A portion of the region $X_t(\partial V)$.

Finally the geometric factor τ is defined on $L_t(\partial V)$ as in equation (II.2.13). From the definitions, it is obvious that

$$A^*(V) = A(V) + \int_{I_t(V)} a'\, dV + \int_{X_t(\partial V)} \Theta a'\, dV \quad . \tag{2.6}$$

The integral over $I_t(V)$ may be done by iteration: first along the normal and then over the surface $\Sigma_t(V)$. Let $\vec{r}(\xi^1,\xi^2)$ be a parametrization of Σ_t or part thereof, such that $\vec{n}\cdot(\frac{\partial\vec{r}}{\partial\xi^1}\times\frac{\partial\vec{r}}{\partial\xi^2}) > 0$. The neighboring three-dimensional space may be parametrized by

$$\vec{R}(\xi^1,\xi^2,\zeta) = \vec{r}(\xi^1,\xi^2) + \zeta\vec{n}(\xi^1,\xi^2) \ .$$

In terms of $\bar{u}_1 = \frac{\partial\vec{r}}{\partial\xi^1}$ and $\bar{u}_2 = \frac{\partial\vec{r}}{\partial\xi^2}$, the area element on Σ_t may be expressed as $dA = \vec{n}\cdot(\bar{u}_1\times\bar{u}_2)\, d\xi^1 d\xi^2$. On the other hand, it follows from eq.(II.1.10) that $\frac{\partial\vec{R}}{\partial\xi^\alpha} = \bar{u}_\alpha - \zeta S(\bar{u}_\alpha)$, while $\frac{\partial\vec{R}}{\partial\zeta} = \vec{n}$, so that the jacobian $J = \frac{\partial\vec{R}}{\partial\zeta}\cdot(\frac{\partial\vec{R}}{\partial\xi^1}\times\frac{\partial\vec{R}}{\partial\xi^2})$ is given by

$$\begin{aligned} J &= \vec{n}\cdot\{\bar{u}_1\times\bar{u}_2 - \zeta[\bar{u}_1\times S(\bar{u}_2) - \bar{u}_2\times S(\bar{u}_1)] + \zeta^2 S(\bar{u}_1)\times S(\bar{u}_2)\} \\ &= \vec{n}\cdot(\bar{u}_1\times\bar{u}_2)(1 - 2\zeta H + \zeta^2 K), \end{aligned}$$

where use has been made of eq.(II.1.13), and the volume element is

$$dV = J\, d\xi^1 d\xi^2 d\zeta = (1-2\zeta H+\zeta^2 K)\, d\zeta dA \tag{2.7}$$

where dA is the area element on Σ_t. This is the requisite factorization.

At this stage it is convenient to introduce quantities that will be called *normal moments*. Given a function f defined throughout the material at each instant t, the normal moment of order m of f, $\langle f\rangle_m$, is the function defined on Σ_t by

$$\langle f\rangle_m(\vec{p}) = \int_{-\delta}^{\delta} \zeta^m f(\vec{p}+\zeta\vec{n}(\vec{p}))\, d\zeta \tag{2.8}$$

where $m = 0,1,2,\ldots$ is any positive integer and $\vec{p} \in \Sigma_t$. The normal moments of the deviations a', σ', $\vec{J}'$ (defined by eq.(2.1)) turn out to be natural building blocks for the theory. They will be attributed special symbols

$$a_m \equiv \langle a' \rangle_m \ , \ \sigma_m \equiv \langle \sigma' \rangle_m \ , \ \vec{J}_m \equiv \langle \vec{J}' \rangle_m \ . \tag{2.9}$$

The vector $\vec{J}_m$ will be decomposed into its normal and tangential parts :

$$\vec{J}_m = \bar{J}_m + j_m^{\perp} \vec{n} \quad (\bar{J}_m \cdot \vec{n} = 0) \ . \tag{2.10}$$

We emphasize that a_m, σ_m and $\vec{J}_m$ are functions defined on Σ_t only. Many equations will be simplified by introducing the following functions also defined on Σ_t:

$$a_s \equiv a_0 - 2Ha_1 + Ka_2 \tag{2.11}$$

$$\sigma_s \equiv \sigma_0 - 2H\sigma_1 + K\sigma_2 \tag{2.12}$$

For a reason that will be clear shortly, they will be called *surface densities*.

Using eqs.(2.7) and (2.9), it follows immediately that

$$\int_{I_t(V)} a' \, dV = \int_{\Sigma_t(V)} (a_0 - 2Ha_1 + Ka_2) \, dA = \int_{\Sigma_t(V)} a_s \, dA$$

so that eq.(2.6) may be rewritten as

$$A^*(V) = A(V) + \int_{\Sigma_t(V)} a_s \, dA + \int_{X_t(\partial V)} \Theta a' \, dV \ . \tag{2.13}$$

An identical equation obviously holds for the internal production:

$$P^*(V) = P(V) + \int_{\Sigma_t(V)} \sigma_s \, dA + \int_{X_t(\partial V)} \Theta \sigma' \, dV \ . \tag{2.14}$$

Thus the total amount of an attribute in V is seen to be

the sum of a bulk contribution from the schematic density, of a surface excess and of a fringe effect. The latter, which is represented by the last integral in eq.(2.13), depends on the shape of $\Delta_t(\partial V)$; it vanishes when $\Delta_t(\partial V) = \beta_t^{\perp}(\partial V)$.

An equation similar to eq.(2.13) will now be obtained for the flux $\Phi^*(\partial V)$. The starting point is the obvious relation

$$\Phi^*(\partial V) = \Phi(\partial V) + \Phi'(\partial V) \ . \tag{2.15}$$

Since the deviation $\vec{J}'$ vanishes everywhere on ∂V except on the strip $\Delta_t(\partial V)$, the last term may be rewritten as

$$\Phi'(\partial V) = \int_{\Delta_t(\partial V)} \vec{J}' \cdot \vec{N} \, dA \ .$$

In order to extract a line flux through $L_t(\partial V)$, this equation is rewritten as

$$\Phi'(\partial V) = \int_{\beta_t^{\perp}(\partial V)} \vec{J}' \cdot \vec{N}^* \, dA + \int_{\Delta_t(\partial V)} \vec{J}' \cdot \vec{N} \, dA - \int_{\beta_t^{\perp}(\partial V)} \vec{J}' \cdot \vec{N}^* \, dA \ . \tag{2.16}$$

The first term on the right can be expressed in terms of the first two normal moments of $\vec{J}'$. Let $\vec{r}(\lambda)$ represent the arc-length parametrization of $L_t(\partial V)$, with orientation such that $\frac{d\vec{r}}{d\lambda} = \overline{T}$, where $\overline{T}$ has been defined previously. An obvious parametrization of $\beta_t^{\perp}(\partial V)$ is then

$$\vec{\rho}(\lambda,\zeta) = \vec{r}(\lambda) + \zeta \vec{n}(\lambda) \ . \tag{2.17}$$

It follows from eq.(II.1.10) that $\frac{\partial \vec{\rho}}{\partial \lambda} = \overline{T} - \zeta S(\overline{T})$, while $\frac{\partial \vec{\rho}}{\partial \zeta} = \vec{n}$ so that

$$\vec{N}^* = \left| \frac{\partial \vec{\rho}}{\partial \lambda} \times \frac{\partial \vec{\rho}}{\partial \zeta} \right|^{-1} \frac{\partial \vec{\rho}}{\partial \lambda} \times \frac{\partial \vec{\rho}}{\partial \zeta}$$

$$= |[\bar{T}-\zeta S(\bar{T})]\times\vec{n}|^{-1}\,[\bar{T}-\zeta S(\bar{T})]\times\vec{n}$$

or

$$\vec{N}^* = -\vec{n}\times\frac{[\bar{T}-\zeta S(\bar{T})]}{|\bar{T}-\zeta S(\bar{T})|} \quad . \tag{2.18}$$

Using $dA = |\frac{\partial\vec{\rho}}{\partial\lambda}\times\frac{\partial\vec{\rho}}{\partial\zeta}|\,d\lambda d\zeta = |\bar{T}-\zeta S(\bar{T})|\,d\lambda d\zeta$ together with eqs.(2.9) and (2.10), we then get

$$\int_{\beta_t^{\perp}(\partial V)}\vec{J}'\cdot\vec{N}^*\,dA = \int_{L_t(\partial V)}d\lambda\int_{-\delta}^{\delta}d\zeta\;|\bar{T}-\zeta S(\bar{T})|\;\vec{J}'\cdot\{-\vec{n}\times\frac{[\bar{T}-\zeta S(\bar{T})]}{|\bar{T}-\zeta S(\bar{T})|}\}$$

$$= \int_{L_t(\partial V)}\bar{j}_0\cdot\bar{v}\,d\lambda + \int_{L_t(\partial V)}\bar{j}_1\cdot[\vec{n}\times S(\bar{T})]\,d\lambda \quad . \tag{2.19}$$

Now if $\bar{u}$ is any vector tangent to Σ_t at a point of $L_t(\partial V)$, it follows, using the self-adjointness of S, that

$$\bar{u}\cdot[\vec{n}\times S(\bar{T})] = S(\bar{T})\cdot(\bar{u}\times\vec{n}) = \bar{T}\cdot S(\bar{u}\times\vec{n})$$

$$= (\vec{n}\times\bar{T})\cdot[\vec{n}\times S(\bar{u}\times\vec{n})] = -\bar{v}\cdot[\vec{n}\times S(\bar{u}\times\vec{n})] \quad .$$

It is easily seen that the linear operator $\tilde{S} : \bar{u} \to -\vec{n}\times S(\bar{u}\times\vec{n})$ has the same eigenvectors as S but with eigenvalues permuted and multiplied by -1. Hence, from eq.(II.1.13),

$$\tilde{S} = S - 2HI \tag{2.20}$$

where I is the identity operator. The above equation may then be rewritten as

$$\bar{u}\cdot[\vec{n}\times S(\bar{T})] = \bar{v}\cdot\tilde{S}(\bar{u}) \quad . \tag{2.21}$$

The operator $\tilde{S}$ will occur frequently in the following developments. Its physical dimension is that of a curvature. We note that, since S is a zero of its characteristic polynomial, $S^2 - 2HS + KI = 0$,

so that

$$S\tilde{S} = -KI . \tag{2.22}$$

Combining eqs.(2.19),(2.21) gives

$$\int_{\beta_t^{\perp}(\partial V)} \vec{J}' \cdot \vec{N}^* \, dA = \int_{L_t(\partial V)} [\bar{J}_0 + \tilde{S}(\bar{J}_1)] \cdot \bar{\nu} \, d\lambda . \tag{2.23}$$

Let us now return to eq.(2.16). By considering separately the parts of $X_t(\partial V)$ contained in M_t^+ and M_t^-, dividing each if necessary into a finite number of regions throughout which the function Θ is constant, and remembering that the deviations vanish on $\Sigma_t^{-\delta}$ and Σ_t^{δ}, it is easily shown that

$$\int_{\Delta_t(\partial V)} \vec{J}' \cdot \vec{N} \, dA - \int_{\beta_t^{\perp}(\partial V)} \vec{J}' \cdot \vec{N}^* \, dA = \int_{X_t(\partial V)} \Theta \, \nabla \cdot \vec{J}' \, dV .$$

Inserting this together with eqs.(2.16) and (2.23), into eq.(2.15) yields

$$\Phi^*(\partial V) = \Phi(\partial V) + \int_{L_t(\partial V)} [\bar{J}_0 + \tilde{S}(\bar{J}_1)] \cdot \bar{\nu} \, d\lambda + \int_{X_t(\partial V)} \Theta \, \nabla \cdot \vec{J}' \, dV . \tag{2.24}$$

This equation is an intermediate result to be used in deriving the surface balance equation in the next section. In preparation for this, one last calculation will be made. From a well-known theorem about integrals over moving volumes (Prager [1973],p.75), it follows that

$$\frac{d}{dt} \int_{X_t(\partial V)} \Theta a' \, dV = \int_{X_t(\partial V)} \Theta \frac{\partial a'}{\partial t} \, dV + \int_{\partial[X_t(\partial V)]} \Theta a' w \, dA \tag{2.25}$$

where w is the normal velocity of the surface $\partial[X_t(\partial V)]$, counted as positive when the enclosed volume expands. The surface $\partial[X_t(\partial V)]$

is made up of $\Delta_t(\partial V)$ and $\beta_t^{\perp}(\partial V)$ on its sides, and of parts of Σ_t^{δ} and $\Sigma_t^{-\delta}$ on its top and bottom. On the latter parts a' vanishes, while on $\Delta_t(\partial V)$ w vanishes because V is fixed in space. This implies that

$$\int_{\partial[X_t(\partial V)]} \Theta a' w \, dA = \int_{\beta_t^{\perp}(\partial V)} \Theta a' w \, dA \quad . \tag{2.26}$$

In order to express this integral in terms of normal moments, we must first find an explicit expression for the normal velocity w of the "belt" $\beta_t^{\perp}(\partial V)$. Intuitively one would expect to see $\frac{d^{\perp}\vec{n}}{dt}$ (= -Grad $v^{\perp}$) coming in. But the final result is not at all obvious. Let t_0 be a given instant at which the integral of eq.(2.26) is to be evaluated and introduce a parametrization $\vec{x}(\lambda,\eta)$ of the strip $\Delta_{t_0}(\partial V)$ such that $\vec{r}(\lambda) = \vec{x}(\lambda,0)$ is the arc-length parametrization of $L_{t_0}(\partial V)$ and $\vec{T}\cdot\frac{\partial \vec{x}}{\partial \eta}(\lambda,0) = 0$ for every λ. When λ is held fixed and η varies, $\vec{x}(\lambda,\eta)$ traces out on ∂V a curve meeting $L_{t_0}(\partial V)$ at right angle. This curve will be called the λ-curve. Now as t progresses in a small interval $(t_0-\varepsilon,t_0+\varepsilon)$, the curve $L_t(\partial V)$ moves on ∂V. For each value of λ, the point of intersection of $L_t(\partial V)$ with the λ-curve will be denoted by $\vec{Q}_\lambda(t)$. At any fixed t in $(t_0-\varepsilon,t_0+\varepsilon)$, the map $\lambda \to \vec{Q}_\lambda(t)$ is a parametrization of $L_t(V)$, from which we may construct a parametrization of the "belt" $\beta_t^{\perp}(\partial V)$:

$$\vec{\rho}(t;\lambda,\zeta) = \vec{Q}_\lambda(t) + \zeta\vec{n}(\vec{Q}_\lambda(t),t) \quad . \tag{2.27}$$

To proceed further, we need the velocity at $t = t_0$ of the point $\vec{Q}_\lambda(t)$ (with fixed λ). To this end, we momentarily abstract ourselves from our present calculation and consider the following question:given a moving surface Σ_t and a *motionless* curve Γ always piercing the

moving surface Σ_t at only one point, what is the velocity of this point of intersection ? To answer this question, let us introduce the arc-length parametrization $\vec{r}(s)$ of Γ and assume that the moving surface Σ_t at time t is represented locally as the set of points $\vec{y}$ such that

$$f(\vec{y},t) = 0 .$$

It follows immediately from this that $v^{\perp} = \dfrac{-\partial f/\partial t}{|\nabla f|}$.

Let us denote by s(t) the Γ-arc-length parameter associated to the point of intersection of Γ and Σ_t. Since $\vec{r}(s(t))$ is on Σ_t at each time t, it follows that $f(\vec{r}(s(t)),t) = 0$ for each t, from which

$$\dot{s}\,\frac{d\vec{r}}{ds}\cdot\nabla f + \frac{\partial f}{\partial t} = 0$$

which, together with the above expression for $v^{\perp}$ gives $\dot{s} = \dfrac{v^{\perp}}{\vec{n}\cdot\dfrac{d\vec{r}}{ds}}$.

The velocity of the point of intersection is then simply

$$\dot{s}\,\frac{d\vec{r}}{ds} = \frac{v^{\perp}}{\vec{n}\cdot\dfrac{d\vec{r}}{ds}}\,\frac{d\vec{r}}{ds} .$$

Coming back to our problem, the curve Γ is now the λ-curve and the moving point of intersection is $\vec{Q}_{\lambda}(t)$. We want its velocity at time t_0. The vector $\dfrac{d\vec{r}}{ds}$ of the general situation above is now clearly $\vec{N}\times\vec{T}$ and it follows from the above equation that

$$\frac{d\vec{Q}_{\lambda}}{dt}(t_0) = \frac{v^{\perp}}{\vec{n}\cdot(\vec{N}\times\vec{T})}\,\vec{N}\times\vec{T} .$$

Now we have $\vec{N} = (\vec{N}\cdot\vec{n})\,\vec{n} + (\vec{N}\cdot\bar{v})\,\bar{v}$ from which $\vec{N}\times\vec{T} = -(\vec{N}\cdot\vec{n})\,\bar{v} + (\vec{N}\cdot\bar{v})\,\vec{n}$

and finally

$$\frac{d\vec{Q}}{dt}_{\lambda}(t_0) = v^{\perp}(\vec{n}-\tau\bar{v}) \qquad (2.28)$$

where τ is defined by eq.(II.2.13). From eqs.(II.1.27),(2.27) and (2.28) it follows that

$$\frac{\partial\vec{\rho}}{\partial t}(t_0,\lambda,\zeta) = v^{\perp}(\vec{n}-\tau\bar{v}) + \zeta[-\mathrm{Grad}\, v^{\perp} + \tau v^{\perp}S(\bar{v})] \quad . \qquad (2.29)$$

It is evident that, when $t = t_0$, the parametrization $\vec{\rho}$ coincides with that defined by eq.(2.17), so that the outward unit normal on the part $\beta^{\perp}_{t_0}(\partial V)$ of $\partial[X_{t_0}(\partial V)]$ is $-\Theta\vec{N}^*$, where $\vec{N}^*$ is given by eq.(2.18). It follows that w may be written as

$$w = -\Theta\vec{N}^* \cdot \frac{\partial\vec{\rho}}{\partial t}(t_0;\lambda,\zeta)$$

$$= \frac{-\Theta}{|\bar{T}-\zeta S(\bar{T})|}\,[\tau v^{\perp}(1-2\zeta H+\zeta^2 K) + \bar{v}\cdot(\zeta I+\zeta^2\tilde{S})(\mathrm{Grad}\, v^{\perp})]\ ,$$

where use has been made of eqs.(2.29),(2.21) and (II.1.13). Inserting this in eq.(2.26), while remembering that $dA = |\bar{T}-S(\bar{T})|d\lambda d\zeta$ on $\beta^{\perp}_t(\partial V)$, and combining the resulting equation with eq.(2.25) yields the desired result:

$$\frac{d}{dt}\int_{X_t(\partial V)} \Theta a'\, dV = \int_{X_t(\partial V)} \Theta\frac{\partial a'}{\partial t}\, dV + \int_{L_t(\partial V)} [\tau v^{\perp} a_s + \bar{v}\cdot[a_1 \mathrm{Grad}\, v^{\perp} + a_2\tilde{S}(\mathrm{Grad}\, v^{\perp})]]d\lambda. \qquad (2.30)$$

3) <u>The first surface balance equation</u>

As the title implies, the balance equation derived in this section is not the only one of its kind. However it is the

most important one because it connects the jumps of the schematic densities with the surface excess densities. The balance equations derived in Chapter IV do not involve the schematic densities and they apply to higher order normal moments. It is remarkable that the first surface balance equation, eventhough it is obtained without making any approximation, is *formally* identical with eq. (II.2.16) obtained in the "empirical" approach. The differences that remain concern the physical interpretation of the surface densities entering into the equations; they disappear in a suitable zeroth order approximation which will later be discussed at length.

The first of eqs.(2.3) guarantees that the balance equation

$$\frac{d}{dt} A^*(V) + \Phi^*(\partial V) - P^*(V) = 0 \qquad (3.1)$$

holds for any region V fixed in space, not intersecting the transition region I_t. The first surface balance equation is essentially a boundary condition equivalent to the requirement that eq.(3.1) shall also hold for any region V fixed in space and encompassing part of the dividing surface.

The first term in eq.(3.1) may be computed with the help of eqs.(2.13) and (2.30), together with the two relations

$$\frac{d}{dt} \int_V a \, dV = \int_{V_t^+} \frac{\partial a^+}{\partial t} \, dV + \int_{V_t^-} \frac{\partial a^-}{\partial t} \, dV - \int_{\Sigma_t(V)} [\![a]\!] \, v^{\perp} \, dA$$

where $V_t^{\pm} = M_t^{\pm} \cap V$ and

$$\frac{d}{dt}\int_{\Sigma_t(V)} a_s\, dA = \int_{\Sigma_t(V)} [\frac{d^\perp a}{dt} s - 2Hv^\perp a_s]\, dA - \int_{L_t(\partial V)} \tau v^\perp a_s\, d\lambda \ , \qquad (3.2)$$

where $\frac{d^\perp}{dt}$ stands for the normal time derivative defined by eq.(II.1.17) and τ is defined by eq.(II.2.13). The first of these two equations is obvious and the second one follows from the general identity expressed by eq.(II.2.42). Using eqs.(2.3) and (2.23), the flux $\Phi^*(\partial V)$ may be written as

$$\Phi^*(\partial V) = \int_{V_t^+} \nabla\cdot\vec{J}^+\, dV + \int_{V_t^-} \nabla\cdot\vec{J}^-\, dV + \int_{\Sigma_t(V)} \{[\![\vec{J}\cdot\vec{n}]\!] + \mathrm{Div}[\vec{J}_0+\tilde{S}(\vec{J}_1)]\}\, dA$$
$$- \int_{X_t(\partial V)} (\frac{\partial a'}{\partial t} - \sigma')\Theta\, dV \ .$$

Substituting the last three equations together with eqs.(2.14) and (2.30) into eq.(3.1) yields

$$\int_{V_t^+} (\frac{\partial a^+}{\partial t} + \nabla\cdot\vec{J}^+ - \sigma^+)\, dV + \int_{V_t^-} (\frac{\partial a^-}{\partial t} - \nabla\cdot\vec{J}^- - \sigma^-)\, dV +$$

$$\int_{\Sigma_t(V)} \{\frac{d^\perp a}{dt} s - 2Hv^\perp a_s + \mathrm{Div}[\vec{J}_0+\tilde{S}(\vec{J}_1)+a_1\,\mathrm{Grad}\, v^\perp + \tilde{S}(a_2\,\mathrm{Grad}\, v^\perp)]$$
$$- \sigma_s + [\![\vec{J}\cdot\vec{n} - av^\perp]\!]\}\, dA = 0 \ ,$$

where we have set $[\![\vec{J}]\!]\cdot\vec{n} - [\![a]\!]v^\perp \equiv [\![\vec{J}\cdot\vec{n} - av^\perp]\!]$. In view of eq.(2.3) and of the arbitrariness of V, this equation is equivalent to

$$\frac{d^\perp a_s}{dt} - 2Hv^\perp a_s + \mathrm{Div}[\vec{J}_0 + \tilde{S}(\vec{J}_1) + a_1\,\mathrm{Grad}\, v^\perp + \tilde{S}(a_2\,\mathrm{Grad}\, v^\perp)]$$
$$- \sigma_s + [\![\vec{J}\cdot\vec{n} - av^\perp]\!] = 0 \qquad (3.3)$$

which is the first surface balance equation. Upon writing

$$\bar{j} \equiv \bar{j}_0 + \tilde{S}(\bar{j}_1) + a_1 \mathrm{Grad}\, v^{\perp} + \tilde{S}(a_2 \mathrm{Grad}\, v^{\perp}) \qquad (3.4)$$

it takes the more compact form

$$\frac{d^{\perp}}{dt} a_s - 2Hv^{\perp} a_s + \mathrm{Div}\, \bar{j} - \sigma_s + [\![\vec{J}\cdot\vec{n} - a v^{\perp}]\!] = 0 . \qquad (3.5)$$

We note that this equation is *formally* identical with the surface balance equation obtained in the empirical approach discussed in Chapter II (eq.(II.2.24)). That a balance equation of exactly the same form as that found in the empirical approach should hold rigourously in the present theory is quite remarkable. For it must be remembered that eqs.(II.2.19-22) which define the surface densities in the empirical approach *do not* rigourously hold in our theory; they are replaced by the more complicated eqs.(2.13), (2.14) and (2.24). The crucial step in the derivation was the decomposition effected in eq.(2.16), leading to eq.(2.24), the last term of which had just the right form to cancel the fringe integrals (integrals over $X_t(\partial V)$) appearing in eqs.(2.14) and (2.30).

This welcomed formal identity of the surface balance equations does not mean however that everything is the same in both descriptions. For one thing, if we look at the surface current density $\bar{j}$ appearing in the surface balance equation of Chapter II (eq.(II.2.24)), we note that it is the same one that is used in computing the surface contribution to the flux $\phi^*(\partial V)$ in eq.(II.2.21). But in the present theory, things are not so simple. The surface current density $\bar{j}$ occuring in eq.(3.5) contains four terms explicited in eq.(3.4), and these do not at all appear in eq.(2.24) which moreover has a more complicated structure than

eq.(II.2.21). To make a definite comparison, we consider a region V, fixed in space, such that at some instant $t, \Delta_t(\partial V) = \beta_t^{\perp}(\partial V)$ (in general, V being motionless, this relation cannot be preserved in the course of time). From eq.(2.24) we have, *for such a particular region at that particular time t*

$$\Phi^*(\partial V) = \Phi(\partial V) + \int_{L_t(\partial V)} [\bar{J}_0 + \tilde{S}(\bar{J}_1)] \cdot \bar{\nu} \, d\lambda$$

without any approximation. On the other hand, the surface current density $\bar{J}$ which occurs in the first surface balance equation (eq.(3.5)) is, according to eq.(3.4), given by

$$\bar{J} \equiv \bar{J}_0 + \tilde{S}(\bar{J}_1) + a_1 \mathrm{Grad}\, v^{\perp} + \tilde{S}(a_2 \mathrm{Grad}\, v^{\perp}) \quad ,$$

which differs from the above integrand by the term $a_1 \mathrm{Grad}\, v^{\perp} + \tilde{S}(a_2 \mathrm{Grad}\, v^{\perp})$. This is in marked contrast with the empirical approach wherein the surface current density used in computing the flux and that occurring in the balance equation are one and the same. The physical interpretation of the term $a_1 \mathrm{Grad}\, v^{\perp} + \tilde{S}(a_2 \mathrm{Grad}\, v^{\perp})$ is easily obtained. At a given instant t_0, let us trace a simple closed curve Γ_{t_0} on Σ_{t_0}. Next let this curve be carried along with the dividing surface in such a way that the velocity of each of its points be always perpendicular to the dividing surface. A new closed curve Γ_t is thus obtained on each Σ_t. Let $\beta^{\perp}(\Gamma_t)$ be the "belt" constructed along the curve Γ_t in the same way that $\beta_t^{\perp}(\partial V)$ was in section 2, and let $I(\Gamma_t)$ be the portion of the transition zone I_t circumscribed by this "belt". The region $I(\Gamma_t)$ is not a fixed region. By considering the balance of the deviation

a' in it, we find, by a slight modification of the argument that led to eq.(2.30), a contribution $-\int_{\Gamma_t} [a_1 \mathrm{Grad}\, v^{\perp} + \tilde{S}(a_2 \mathrm{Grad}\, v^{\perp})]\cdot\bar{\nu}\, d\lambda$ which represents the rate of change of "the amount of a'" contained in $I(\Gamma_t)$ due to the tilting of the "belt" $\beta^{\perp}(\Gamma_t)$, as Σ_t moves and is deformed. The occurrence of the tangent vector $\mathrm{Grad}\, v^{\perp}$ in this context is natural, since according to eq.(II.1.26), $\mathrm{Grad}\, v^{\perp} = -\frac{d^{\perp}\vec{n}}{dt}$.

The relation between eqs.(II.2.19-22) and eqs.(2.13), (2.14) and (2.24) of the present chapter will be elucidated in the next section.

4) The normal moment expansion of fluxes and density integrals

The purpose of this section is to investigate the status of eqs.(II.2.19-22) in the context of the present theory. Our discussion will proceed from the exact relations

$$A^*(V) = \int_V a\, dV + \int_{\Sigma_t(V)} a_s\, dA + \int_{X_t(\partial V)} \Theta a'\, dV \tag{4.1}$$

$$\Phi^*(\partial V) = \int_{\partial V} \vec{J}\cdot\vec{N}\, dA + \int_{\Delta_t(\partial V)} \vec{J}'\cdot\vec{N}\, dA \tag{4.2}$$

that were obtained in section 2. The flux equation will be treated first. Let λ be the arc-length parameter on $L_t(\partial V)$. At a point $\vec{p}(\lambda)$ of this curve, the plane spanned by $\vec{N}$ and $\vec{n}$, or equivalently by $\vec{n}$ and $\bar{\nu}$, cuts $\Sigma_t(V)$ along a normal section $\Gamma_{\bar{\nu}}$. Let η represent the

arc-length along this curve with $\eta = 0$ at $\vec{p}(\lambda)$ and positive values of η in the $\vec{\nu}$ direction. The two parameters λ,η give a parametrization $\vec{r}(\lambda,\eta)$ of a region of $\Sigma_t(V)$ containing $L_t(\partial V)$, which may be extended to a parametrization

$$\vec{R}(\lambda,\eta,\zeta) = \vec{r}(\lambda,\eta) + \zeta\vec{n}(\lambda,\eta) \tag{4.3}$$

of the adjacent three-dimensional space. Given (λ,ζ), let $\tilde{\eta}(\lambda,\zeta)$ be that value of η such that $\vec{R}(\lambda,\eta,\zeta) \in \partial V$. (It is assumed that the geometry of ∂V is simple enough -no folds- that a single η is so defined.) An obvious parametrization of $\Delta_t(\partial V)$ is then

$$\vec{\rho}(\lambda,\zeta) = \vec{R}(\lambda,\tilde{\eta}(\lambda,\zeta),\zeta) \quad , \tag{4.4}$$

in terms of which the area element on $\Delta_t(\partial V)$ is $dA = \Omega(\lambda,\zeta)d\lambda d\zeta$, with $\Omega(\lambda,\zeta) = \left|\frac{\partial\vec{\rho}}{\partial\lambda} \times \frac{\partial\vec{\rho}}{\partial\zeta}\right|$. It follows immediately that

$$\int_{\Delta_t(\partial V)} \vec{J}'\cdot\vec{N}\, dA = \int_{L_t(\partial V)-\delta} d\lambda \int_{-\delta}^{\delta} d\zeta\, \vec{J}'(\vec{\rho}(\lambda,\zeta))\cdot\vec{N}(\lambda,\zeta)\Omega(\lambda,\zeta) \quad . \tag{4.5}$$

It must now be remembered that ∂V is a "macroscopic object". Given the thinness of the transition zone, a first order approximation of $\Omega(\lambda,\zeta)\vec{N}(\lambda,\zeta)$ about $\zeta = 0$ will thus be very accurate. Next note that unless $\vec{N}$ is excessively close to $\vec{n}$ or $-\vec{n}$ at $\vec{p}$, the function $\tilde{\eta}(\lambda,\zeta)$ will differ very little from 0 as ζ ranges over $[-\delta,\delta]$, while for any sensible choice of the dividing surface, the variation of $\vec{J}'\circ\vec{R}(\lambda,\eta,\zeta)$ at fixed (λ,ζ) is slow (macroscopic). Hence, with great accuracy, $\vec{J}'(\vec{\rho}(\lambda,\zeta))$ may be replaced by $\vec{J}'\circ\vec{R}(\lambda,0,\zeta) + \tilde{\eta}(\lambda,\zeta)\frac{\partial}{\partial\eta}(\vec{J}'\circ\vec{R})(\lambda,0,\zeta)$ for $\zeta \in [-\delta,\delta]$. Hence it appears that a negligible error is introduced by writing

$$\int_{\Delta_t(\partial V)} \vec{J}'\cdot\vec{N}\, dA = \int_{L_t(\partial V)} d\lambda \int_{-\delta}^{\delta} [\vec{J}'\circ\vec{R}(\lambda,0,\zeta) + \tilde{n}(\lambda,\zeta)\frac{\partial}{\partial n}(\vec{J}'\circ\vec{R})(\lambda,0,\zeta)]\cdot$$

$$[\Omega(\lambda,0)\vec{N}(\lambda,0) + \zeta\frac{\partial}{\partial\zeta}(\Omega\vec{N})(\lambda,0)]\, d\zeta\ .$$

Discarding terms of order ≥ 2 in ζ, this may be rewritten as

$$\int_{\Delta_t(\partial V)} \vec{J}'\cdot\vec{N}\, dA = \int_{L_t(\partial V)} \{\alpha^{-1}\vec{N}\cdot\vec{J}_0 + \frac{\partial}{\partial\zeta}(\Omega\vec{N})(\lambda,0)\cdot\vec{J}_1 - \alpha^{-1}\tau\vec{N}\cdot D_{\vec{v}}\vec{J}_1\}\, d\lambda \qquad (4.6)$$

where $\alpha = \vec{N}\cdot\vec{v}$, $\tau = \vec{N}\cdot\vec{n}/\vec{N}\cdot\vec{v}$ and $\vec{J}_0$ and $\vec{J}_1$ are as defined by eq.(2.9). We shall see below that this equation represents the zeroth and first order contributions form a systematic expansion of the left-hand side in terms of normal moments of $\vec{J}'$.

Using eq.(2.10) and remembering that $\vec{N}$ lies in the plane spanned by $\vec{n}$ and $\vec{v}$, we find

$$\alpha^{-1}\vec{N}\cdot\vec{J}_0 = \frac{1}{\vec{N}\cdot\vec{v}}(\vec{N}\cdot\vec{n}\vec{n} + \vec{N}\cdot\vec{v}\vec{v})\cdot(\vec{J}_0 + j_0^{\perp}\vec{n})$$

$$= \vec{J}_0\cdot\vec{v} + \tau j_0^{\perp}$$

so that the first term on the right-hand side of eq.(4.4) may be rewritten as

$$\int_{L_t(\partial V)} \alpha^{-1}\vec{N}\cdot\vec{J}_0\, d\lambda = \int_{L_t(\partial V)} (\vec{J}_0\cdot\vec{v} + \tau j_0^{\perp})\, d\lambda\ . \qquad (4.7)$$

This represents the zeroth order contribution to the left-hand side of eq.(4.6). Its mathematical structure is identical to that of the expression used in the empirical approach to compute the flux (eq.(II.2.21)) so that another important link has been established. However in the present theory, $j_0^{\perp}$ is defined as a zeroth order moment by $j_0^{\perp} = \vec{n}\cdot\langle\vec{J}'\rangle_0$ and as of yet we have no equivalent

of eq.(II.2.22) which *defined* $j^{\perp}$ as being equal to $a^{s}v^{\perp}$. We will return to this point in the next chapter.

Equation (4.7) involves actually very little information concerning the geometry of the surface ∂V in the vicinity of Σ_t. As the finer details must be involved in an exact evaluation of the left-hand side of eq.(4.6), the contributions stemming from the higher order moments of $\vec{J}'$ clearly cannot all have this simple form. It is interesting to find the nature of the first order correction, which is contained in the last two terms of eq.(4.6). Unfortunately their computation is surprisingly involved, the complications arising from the term $\frac{\partial\Omega}{\partial\zeta}(\lambda,0)$. We give an outline of the derivation leading to the final result, eq.(4.15). We start from

$$\Omega = \left|\frac{\partial\vec{\rho}}{\partial\lambda}\times\frac{\partial\vec{\rho}}{\partial\zeta}\right| = \sqrt{\left|\frac{\partial\vec{\rho}}{\partial\lambda}\right|^2\left|\frac{\partial\vec{\rho}}{\partial\zeta}\right|^2 - \left(\frac{\partial\vec{\rho}}{\partial\lambda}\cdot\frac{\partial\vec{\rho}}{\partial\zeta}\right)^2} \quad . \tag{4.8}$$

To evaluate $\frac{\partial\Omega}{\partial\zeta}(\lambda,0)$ we need only know $\frac{\partial\vec{\rho}}{\partial\lambda}(\lambda,\zeta)$ and $\frac{\partial\vec{\rho}}{\partial\zeta}(\lambda,\zeta)$ to first order in ζ. From eq.(4.4), it follows that

$$\frac{\partial\vec{\rho}}{\partial\lambda}(\lambda,\zeta) = \frac{\partial\vec{R}}{\partial\lambda}(\lambda,0,0) + \zeta\left[\frac{\partial\tilde{\eta}}{\partial\zeta}\frac{\partial^2\vec{R}}{\partial\eta\partial\lambda} + \frac{\partial^2\vec{R}}{\partial\zeta\partial\lambda} + \frac{\partial^2\tilde{\eta}}{\partial\zeta\partial\lambda}\frac{\partial^2\vec{R}}{\partial\zeta\partial\lambda}\right]\Bigg|_{\eta=\zeta=0} + O(\zeta^2) \tag{4.9}$$

and

$$\frac{\partial\vec{\rho}}{\partial\zeta}(\lambda,\zeta) = \frac{\partial\tilde{\eta}}{\partial\zeta}(\lambda,0)\,\frac{\partial\vec{R}}{\partial\eta}(\lambda,0,0) + \frac{\partial\vec{R}}{\partial\zeta}(\lambda,0,0) + \zeta\left[\frac{\partial^2\tilde{\eta}}{\partial\zeta^2}\frac{\partial\vec{R}}{\partial\eta} + \left(\frac{\partial\tilde{\eta}}{\partial\zeta}\right)^2\frac{\partial^2\vec{R}}{\partial\eta^2} + 2\frac{\partial\tilde{\eta}}{\partial\zeta}\frac{\partial^2\vec{R}}{\partial\eta\partial\zeta} + \frac{\partial^2\vec{R}}{\partial\zeta^2}\right]\Bigg|_{\eta=\zeta=0} + O(\zeta^2) \quad . \tag{4.10}$$

The partial derivatives of $\vec{R}$ are easily evaluated. Denoting by

κ the curvature function of Σ_t (eq.(II.1.12)) and using the Gauss equation (eq.(II.1.14)), we find from eq.(4.3)

$$\frac{\partial\vec{R}}{\partial\lambda}(\lambda,0,0) = \bar{T}\ ,\ \frac{\partial\vec{R}}{\partial\eta}(\lambda,0,0) = \bar{\nu}\ ,\ \frac{\partial\vec{R}}{\partial\zeta}(\lambda,0,0) = \vec{n}$$

$$\frac{\partial^2\vec{R}}{\partial\lambda^2}(\lambda,0,0) = \bar{\nabla}_{\bar{T}}\bar{T} + \kappa(\bar{T})\,\vec{n}\ ,\ \frac{\partial^2\vec{R}}{\partial\eta^2}(\lambda,0,0) = \kappa(\bar{\nu})\,\vec{n}\ ,\ \frac{\partial^2\vec{R}}{\partial\zeta^2}(\lambda,0,0) = \vec{0}$$

$$\frac{\partial^2\vec{R}}{\partial\lambda\partial\eta}(\lambda,0,0) = \bar{\nabla}_{\bar{T}}\bar{\nu} + \bar{T}\cdot S(\bar{\nu})\,\vec{n}\ ,\ \frac{\partial^2\vec{R}}{\partial\lambda\partial\zeta}(\lambda,0,0) = -S(\bar{T})\ ,\ \frac{\partial^2\vec{R}}{\partial\eta\partial\zeta}(\lambda,0,0) = -S(\bar{\nu})\ .$$

The partial derivatives of $\tilde{\eta}$ are a bit trickier to evaluate. Let ∂V be described locally by the equation $F(\vec{r}) = 0$. Then for any λ,ζ, $F(\vec{R}(\lambda,\tilde{\eta}(\lambda,\zeta),\zeta)) = 0$, from which

$$\nabla F \cdot \left[\frac{\partial\tilde{\eta}}{\partial\zeta}(\lambda,0)\,\frac{\partial\vec{R}}{\partial\eta}(\lambda,0,0) + \frac{\partial\vec{R}}{\partial\zeta}(\lambda,0,0)\right] = 0$$

and thence

$$\frac{\partial\tilde{\eta}}{\partial\zeta}(\lambda,0) = -\frac{\vec{N}\cdot\vec{n}}{\vec{N}\cdot\bar{\nu}} = -\tau\ .$$

To compute $\frac{\partial^2\tilde{\eta}}{\partial\zeta^2}(\lambda,0)$, we use eq.(4.4) to get

$$\begin{aligned}\frac{\partial^2\vec{\rho}}{\partial\zeta^2}(\lambda,\zeta) &= 2\frac{\partial\tilde{\eta}}{\partial\zeta}(\lambda,\zeta)\,\frac{\partial^2\vec{R}}{\partial\zeta\partial\eta}(\lambda,\tilde{\eta}(\lambda,\zeta),\zeta)\\ &\quad + \left(\frac{\partial\tilde{\eta}}{\partial\zeta}\right)^2\frac{\partial^2\vec{R}}{\partial\eta^2}(\lambda,\tilde{\eta}(\lambda,\zeta),\zeta) + \frac{\partial^2\tilde{\eta}}{\partial\zeta^2}\frac{\partial\vec{R}}{\partial\eta}(\lambda,\tilde{\eta}(\lambda,\zeta),\zeta)\\ &\quad + \frac{\partial^2\vec{R}}{\partial\zeta^2}(\lambda,\tilde{\eta}(\lambda,\zeta),\zeta)\end{aligned}$$

from which

$$\frac{\partial^2\vec{\rho}}{\partial\zeta^2}(\lambda,0) = 2\tau S(\bar{\nu}) + \tau^2\kappa(\bar{\nu})\,\vec{n} + \frac{\partial^2\tilde{\eta}}{\partial\zeta^2}(\lambda,0)\,\bar{\nu}\ . \qquad (4.11)$$

An independent expression for $\frac{\partial^2\vec{\rho}}{\partial\zeta^2}(\lambda,0)$ will allow us to solve for $\frac{\partial^2\tilde{\eta}}{\partial\zeta^2}(\lambda,0)$. Let us denote the covariant derivative on ∂V by $\bar{\nabla}'$ and the shape operator of ∂V by S', and write $\vec{u} \equiv \frac{\partial\vec{\rho}}{\partial\zeta}$. From the Gauss

equation it follows that

$$\frac{\partial^2 \vec{\rho}}{\partial \zeta^2} = \bar{\nabla}'_{\vec{u}} \vec{u} + \vec{u} \cdot S'(\vec{u}) \vec{N} .$$

But $$\frac{\partial \vec{\rho}}{\partial \zeta}(\lambda,0) = -\tau \bar{v} + \vec{n} = \frac{\vec{U}}{\vec{N} \cdot \bar{v}} \tag{4.12}$$

where $$\vec{U} \equiv \vec{N} \times \bar{T} \tag{4.13}$$

so that

$$\frac{\partial^2 \vec{\rho}}{\partial \zeta^2}(\lambda,0) = \bar{\nabla}'_{\vec{u}} \vec{u} + \frac{1}{(\vec{N} \cdot \bar{v})} \kappa'(\vec{U}) \vec{N} .$$

Combining this last result with eq.(4.11) and taking the dot product with $\vec{N}$ yields

$$\frac{1}{(\vec{N} \cdot \bar{v})^2} \kappa'(\vec{U}) = 2\tau \vec{N} \cdot S(\bar{v}) + \tau^2 \kappa(\bar{v}) \vec{N} \cdot \vec{n} + \vec{N} \cdot \bar{v} \frac{\partial^2 \mathfrak{R}}{\partial \zeta^2}(\lambda,0) ,$$

from which

$$\frac{\partial^2 \mathfrak{R}}{\partial \zeta^2}(\lambda,0) = \frac{1}{(\vec{N} \cdot \bar{v})^3} [\kappa'(\vec{U}) + \vec{N} \cdot \vec{n} (1 + (\vec{N} \cdot \bar{v})^2) \kappa(\bar{v})] . \tag{4.14}$$

Substituting all these expressions in eqs.(4.9) and (4.10), we find that the right-hand side of eq.(4.8) is, to first order in ζ, given by

$$\Omega(\lambda,\zeta) = \frac{1}{\vec{N} \cdot \bar{v}} + \frac{\zeta}{\vec{N} \cdot \bar{v}} [-\kappa(\bar{T}) + \tau^2 \kappa(\bar{v}) - \tau \bar{T} \cdot \bar{\nabla}_{\bar{T}} \bar{v} - \frac{\tau}{\vec{N} \cdot \bar{v}} \kappa'(\vec{U})] + O(\zeta^2) .$$

On the other hand we have from eq.(II.1.10)

$$\frac{\partial \vec{N}}{\partial \zeta}(\lambda,0) = D_{\vec{u}} \vec{N} = -S'(\vec{u})$$

where $\vec{u} \equiv \frac{\partial \vec{\rho}}{\partial \zeta}(\lambda,0)$, so that from eq.(4.12)

$$\frac{\partial \vec{N}}{\partial \zeta}(\lambda,0) = -\frac{1}{\vec{N} \cdot \bar{v}} S'(\vec{U}) .$$

Together with the above expression for Ω, this gives

$$\frac{\partial(\Omega\vec{N})}{\partial\zeta}(\lambda,0) = (\vec{N}\cdot\bar{v})^{-1}\,[-\kappa(\bar{T}) + \tau^2\kappa(\bar{v}) + \tau\,\bar{v}\cdot\bar{\nabla}_{\bar{T}}\bar{T} - \tau(\vec{N}\cdot\bar{v})^{-1}\kappa'(\hat{U})]\,\vec{N}$$

$$- (\vec{N}\cdot\bar{v})^{-2}\,S'(\hat{U})\ .$$

Inserting this in eq.(4.6) and developing the last term in the latter we finally obtain

$$\int_{\Delta_t(\partial V)} \vec{J}'\cdot\vec{N}\,dA = \int_{L_t(\partial V)} (\bar{J}_0\cdot\bar{v} + \tau j_0^{\perp})\,d\lambda$$

$$+ \int_{L_t(\partial V)} [\gamma(\bar{J}_1\cdot\bar{v} + \tau j_1^{\perp}) - \tau\bar{v}\cdot(\Omega_1(\bar{v}) + \tau\bar{\omega}_1) - (\vec{N}\cdot\bar{v})^{-2}\,S'(\hat{U})\cdot(\bar{J}_1 + j_1^{\perp}\vec{n})]\,d\lambda$$

$$+ \text{terms of order} \geq 2\ , \qquad (4.15)$$

where

$$\gamma \equiv -\kappa(\bar{T}) + \tau^2\kappa(\bar{v}) + \tau\,\bar{v}\cdot\bar{\nabla}_{\bar{T}}\bar{T} - \tau(\vec{N}\cdot\bar{v})^{-1}\kappa'(\hat{U})\ ,$$

$$\Omega_1 \equiv \bar{\nabla}\bar{J}_1 - j_1^{\perp}S\ ,\quad \bar{\omega}_1 \equiv S(\bar{J}_1) + \mathrm{Grad}\,j_1^{\perp}\ .$$

The first term of the first order correction in eq.(4.15) (last integral) has a structure reminiscent of the zeroth order contribution but the analogy is lost in the other two terms. Hence, from the point of view of the present theory, the expression (equation (II.2.21)) used in the empirical approach to compute the line flux is a zeroth order approximation.

The derivation of eq.(4.6) presented above was meant to show clearly the physical ideas that justify a first or zeroth order approximation. It is possible to take a more formal approach and obtain a systematic expansion of eq.(4.5) in terms of the normal moments of the deviation $\vec{J}'$. The result is:

$$\int_{\Delta_t(\partial V)} \vec{J}'\cdot\vec{N}\,dA = \sum_{m=0}^{\infty} \int_{L_t(\partial V)} \vec{\Delta}_m\cdot\vec{J}_m\,d\lambda \qquad (4.16)$$

where $\vec{J}_m$ is given by eq.(2.9) and the differential operator $\vec{\Delta}_m$ is defined by

$$\vec{\Delta}_m = \sum_{k=0}^{m} \vec{A}_m^k (D_{\bar{v}})^k \tag{4.17}$$

with $$\vec{A}_m^k = \sum_{q+\ell+n=m} a_q \Gamma_\ell^k \vec{N}_n . \tag{4.18}$$

The expressions occurring in this sum are defined through the following equations

$$\begin{aligned} \Omega(\lambda,\zeta) &= \sum_{q=0}^{\infty} a_q(\lambda)\,\zeta^q \\ [\eta(\lambda,\zeta)]^k &= \sum_{\ell=0}^{\infty} \Gamma_\ell^k(\lambda)\,\zeta^\ell \qquad (\Gamma_\ell^k = 0 \text{ for } \ell<k) \\ \vec{N}(\lambda,\zeta) &= \sum_{n=0}^{\infty} \zeta^n \vec{N}_n(\lambda) \quad . \end{aligned} \tag{4.19}$$

The zeroth and first order terms in eq.(4.16) agree with eq.(4.15).

The fringe integral in eq.(4.1) may be analyzed along similar lines. Using the same parametrization as above, let

$$\Gamma(\lambda,\eta) = \left| \frac{\partial \vec{r}}{\partial \lambda} \times \frac{\partial \vec{r}}{\partial \eta} \right|$$

and $$\Lambda(\lambda,\eta,\zeta) = 1 - 2\zeta H(\lambda,\eta) + \zeta^2 K(\lambda,\eta) \quad .$$

It is then a simple matter to show that

$$\int_{X_t(\partial V)} \Theta a' \, dV = \int_{L_t(\partial V)} d\lambda \int_{-\delta}^{\delta} d\zeta \int_0^{\bar{\eta}(\lambda,\zeta)} d\eta \; \Gamma(\lambda,\eta)\Lambda(\lambda,\eta,\zeta)a'(\lambda,\eta,\zeta) \quad .$$

It follows from this equation that

$$\int_{X_t(\partial V)} \Theta a' \, dV = \int_{L_t(\partial V)} \alpha(\lambda)\, d\lambda \tag{4.20}$$

with $$\alpha = -\tfrac{1}{2}a_1 + \sum_{\ell=2}^{\infty} [D^{(\ell)}\Gamma - 2D^{(\ell-1)}\bar{H} + D^{(\ell-2)}\bar{K}]\, a_\ell \quad , \tag{4.21}$$

where $\hat{\Gamma}$,$\hat{H}$ and $\hat{K}$ are the operators of multiplication by Γ,H and K respectively and the differential operator $D^{(m)}$ is defined by

$$D^{(m)} = \sum_{k=0}^{m} \frac{1}{(k-1)!} \Gamma_m^{k+1} (D_{\bar{v}})^k \quad .$$

It follows from eq.(4.21) that the fringe effect expressed by eq.(4.20) involves only the normal moments of a' of order ≥ 1. Thus, to zeroth order, the fringe integral vanishes.

The conclusion that may be drawn at this point is that when all normal moments of order ≥ 1 can be neglected, a complete correspondence is achieved with the empirical approach. For not only the surface balance equation but also the expressions for $A^*(V)$ and $\Phi^*(\partial V)$ then have identical structures in both approaches. Indeed, on retaining only the zeroth order term in eq.(4.16), the left-hand side is approximated by the right-hand side of eq.(4.7), which has exactly the same structure as the expression (eq. (II.2.21)) used in the empirical approach to compute the line flux. Likewise, on neglecting all moments of order ≥ 1, the last term in eq.(4.1) vanishes and we are left with an expression of the same form as that used in the empirical approach (eq.(II.2.19)) to represent the surface contribution to $A^*(V)$.

In situations where the first (or higher) order normal moments would play a role, the correspondence would no longer be complete. For, although the surface balance equations would still be formally identical, the expressions used to compute $A^*(V)$ and $\Phi^*(\partial V)$ would then be different in both approaches, and the surface current density $\bar{j}$ appearing in the surface balance equation would

no longer have as simple a physical interpretation as that found in the empirical approach (eq.(II.2.21)).

To round up the connection with the empirical approach we shall also have to look for an interpretation of eq.(II.2.22) in the context of the general theory. We will find it when we consider balance equations for higher order moments in the next chapter.

5) The information contained in the normal moments.

In this section, we shall briefly comment on the information contained in the normal moments. We write $f(\zeta) = a'(\vec{p}+\zeta\vec{n}(\vec{p}))$, where a' is the deviation defined by eq.(2.1), and introduce the change of variables $x = \zeta/\delta$, $g(x) = f(x\delta)$, so that $\langle f\rangle_m = \delta^{m+1}\int_{-1}^{1} g(x)x^m\,dx \equiv \delta^{m+1}\langle g\rangle_m$. In terms of the scalar product $(\ ,\ )$ on the Hilbert space $L^2[-1,1]$ (Reed and Simon [1972]), we have $\langle g\rangle_m = (g,x^m)$. (The function g, being bounded on [-1,1], clearly belongs to this space.) Knowledge of all the moments $\langle g\rangle_m$ enables one to compute the scalar product of g with any Legendre polynomial, and therefore determines g uniquely. Hence knowing all the moments $\langle g\rangle_m$ is equivalent to knowing g itself. However the information contained in the full sequence $(\langle g\rangle_m)_{m\in N}$ is mathematically redundant. For it is easily deduced from the Müntz theorem (Schwartz [1959]) that given any fixed integer $m_0 \geq 0$, the sequence

of functions $(x^m)_{m\geq m_0}$ is total in the space $L^2[-1,1]$. It follows that mere knowledge of all moments $\langle g\rangle_m$ with $m \geq m_0$ suffices to determine g uniquely. An immediate consequence is that if a function $g \in L^2[-1,1]$ satisfies $\langle g\rangle_m = 0$ for every $m \geq m_0$, then $g = 0$, *and this no matter how large m_0 is*! This state of affairs results from the fact that the vectors x^m are not topologically linearly independent in $L^2[-1,1]$, in the sense that any one of them can be written as a L^2-converging series in terms of the others and actually in infinitely many ways.

The aim of the Gibbs approach is to extract gross features of the interfacial structure that are sufficient to describe its influence on the bulk fields. The first few normal moments of the deviations are adequate for that. As stated above, the full sequence of moments contains all the detailed information about the exact densities. But with mere knowledge of the first few moments, it is to be expected that some questions cannot be answered. Consider for example a flat dividing surface Σ_t, and suppose that we wish to compute a flux $\Phi^*(S)$ through a flat surface S *parallel* to Σ_t. As long as S lies outside the transition zone I_t, this flux may be computed using the bulk current density $\vec{J}$. But with mere knowledge of the first few moments $\vec{J}_0, \vec{J}_1, \ldots$ it is strictly impossible to compute this flux when S lies inside the transition zone I_t. The most favorable situation is at the other extreme when S meets Σ_t at right angle everywhere, that is when $\vec{N} = \vec{\nu}$ or equivalently $\vec{N}\cdot\vec{n} = 0$ all along the curve $S\cap\Sigma_t$.

The more $\vec{N}$ receeds away from $\bar{v}$, the less accurate becomes the zeroth order approximation expressed by eq.(4.7). This failure of the approximation is already manifest in the behavior of the factor τ which goes to infinity as $\vec{N}$ approaches $\vec{n}$. Note that the same divergence is present in the empirical approach (eq.(II.2.21)). In that context it may be understood in purely geometrical terms. Consider for instance a flat dividing surface Σ_t and take for the region V a cone fixed in space, with axis perpendicular to Σ_t. In the empirical approach, the term $\tau a^s v^\perp$ arises from a purely convective effect: it represents the flow of the surface excess a^s through ∂V, as this excess is carried along with the dividing surface Σ_t. It is clear that the rate of this convective transport becomes greater as the aperture of the cone increases. When the aperture is close to 180°, a small displacement of Σ_t can indeed produce a dramatic change of the area of the enclosed patch $\Sigma_t(V)$, meaning that a large amount of surface excess has crossed the boundary ∂V, in a very short time. In fact, for a given normal velocity of Σ_t, it is geometrically obvious that the rate of transport through the boundary via this mechanism goes to infinity as the aperture of the cone goes to 180° without reaching it. This divergence in the empirical approach is embodied in the geometrical factor τ appearing in eq.(II.2.21). It is a by-product of the idealization implied in using excess densities concentrated on a surface. In a real system this divergence cannot occur. The fact that it is also present in the zeroth order approx-

imation of the rigorous theory in eq.(4.7) simply means that this approximation is no longer good enough to compute the flux when $\vec{N}$ becomes too close to $\vec{n}$. The nature of the approximation is best understood by considering plane surfaces. The situation is illustrated in Fig.3, which shows a section of the surfaces Σ_t and S. The distance perpendicular to the plane of the figure is measured by λ, and the unit normal to this plane is $\bar{\tau} = \vec{n} \times \bar{v}$. The curve $S \cap \Sigma_t$ is denoted by Γ. The position vector of a point of the part of S comprised between $\Sigma_t^{-\delta}$ and Σ_t^{δ} may be written as

$$\begin{aligned} \vec{\rho}(\lambda,\zeta) &= \lambda\bar{\tau} + \zeta\vec{n} - \zeta \cot\theta\, \bar{v} \\ &= \lambda\bar{\tau} + \zeta\vec{n} - \tau\zeta\bar{v} \end{aligned} \qquad (5.1)$$

and the area element on S is clearly $dA = \frac{d\lambda d\zeta}{\sin\theta} = \frac{d\lambda d\zeta}{\vec{N}\cdot\bar{v}}$.

It follows that

$$\int_S \vec{J}'\cdot\vec{N}\, dA = \int_\Gamma \int_{-\delta}^{\delta} \vec{J}'(\lambda\bar{\tau} + \zeta\vec{n} - \tau\zeta\bar{v})\cdot\vec{N}\, \frac{d\lambda d\zeta}{\vec{N}\cdot\bar{v}} .$$

The last term in eq.(5.1) represents a displacement parallel to Σ_t. Its largest norm in the region of interest is $\tau\delta$. If the variation of $\vec{J}'$ along that direction and over this distance may be neglected, we have

$$\begin{aligned} \int_S \vec{J}'\cdot\vec{N}\, dA &\simeq \int_\Gamma \int_{-\delta}^{\delta} \vec{J}'(\lambda\bar{\tau} + \zeta\vec{n})\cdot\vec{N}\, \frac{d\lambda d\zeta}{\vec{N}\cdot\bar{v}} \\ &= \int_\Gamma \langle\vec{J}'\rangle_0\cdot\vec{N}\, \frac{d\lambda}{\vec{N}\cdot\bar{v}} = \int_\Gamma (\bar{J}_0\cdot\bar{v} + \tau j_0^{\perp})\, d\lambda \end{aligned}$$

where we have used $\langle\vec{J}'\rangle_0 = \bar{J}_0 + j_0^{\perp}\vec{n}$ and $\vec{N} = (\vec{N}\cdot\vec{n})\vec{n} + (\vec{N}\cdot\bar{v})\bar{v}$.

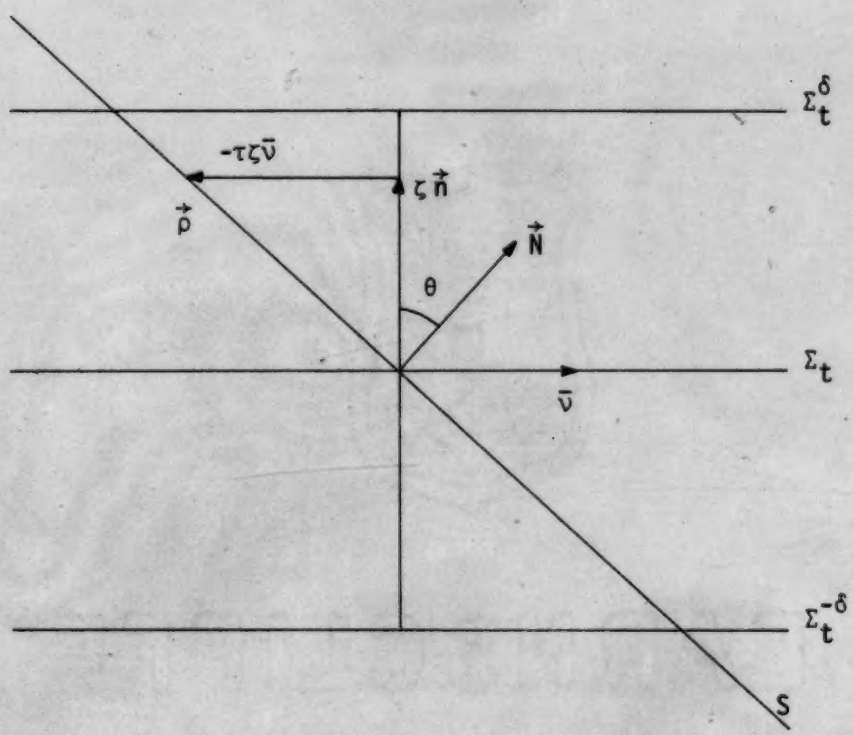

Figure 3: The zeroth order current excess for flat surfaces.

This is identical with our zeroth order approximation. Hence we see that, in this case, the zeroth order approximation consists simply in neglecting the variation of $\vec{J}'$ parallel to Σ_t over a distance $\tau\delta$. The smaller θ, the smaller is this distance and the better is the approximation. The smallness of δ ensures its validity when $\vec{N}$ is not excessively close to $\vec{n}$. This simple argument would break down for a curved dividing surface. However it follows from eq.(4.15) that the curvature effects leave the zeroth order contribution unaffected and make their first appearance in the first order correction. This correction takes into account the curvatures of both Σ_t and S, but also keeps track, to first order, of the lateral variation of $\vec{J}'$: this may be seen through the expressions of $\bar{\omega}_1$ and Ω_1 following eq.(4.15). It is clear from Fig.3 that, as θ decreases or equivalently as τ increases, the lateral variation of $\vec{J}'$ may play a greater role, which means that higher order terms in eq.(4.16) begin to contribute, and higher order moments are needed. The structure of the first order correction in eq.(4.15) is however already quite complicated, so that higher order corrections are not worth considering.

The purpose of this discussion was not to cast a doubt on the validity of the expressions obtained in the previous section. In fact, the thinness of the transition zone ensures them a wide range of validity. Instead we deliberately considered an extreme situation - probably devoid of any practical interest - just to show what kind of information cannot be extracted from

the first few moments. In conclusion we emphasize that it is only the approximate expressions used to compute fluxes or density integrals that are subject to possible limitations; the first surface balance equation (eq.(3.3)) is exact and applies without qualifications.

6) Vector balance equations

With a view towards the momentum balance considered in Chapter V, we now deduce the easy transposition of the first surface balance equation to the vector case. The idea is very simple: if $\vec{e}$ is some constant vector and $\vec{A}$ is some vector attribute, then $\vec{e} \cdot \vec{A}$ is a scalar attribute and as such, has densities which must obey the first surface balance equation (eq.(3.3)). If the schematic density is denoted by $\vec{a}$ and the exact density by $\vec{a}^*$, the various moments $\vec{a}_m$ are defined by applying eq.(2.9), a' being replaced by $\vec{a}' \equiv \vec{a}^* - \vec{a}$. As noted in Section 2 of Chapter II, the bulk current density associated to $\vec{e} \cdot \vec{a}$ may be written as $M(\vec{e})$ for some linear operator field M. The deviation between exact M, which we denote by M_* and not M^* to avoid confusion with the adjoint of M, is $M' = M_* - M$ and its normal moments M_m are defined in the usual fashion. Denoting by $\vec{J}_{\vec{e}}$ the surface current density associated to $\vec{e} \cdot \vec{a}_s$, we have from eq.(3.4)

$$\vec{J}_{\vec{e}} = PM_0(\vec{e}) + \tilde{S}PM_1(\vec{e}) + \vec{e}\cdot\vec{a}_1 \operatorname{Grad} v^{\perp} + \vec{e}\cdot\vec{a}_2 \tilde{S}(\operatorname{Grad} v^{\perp})$$

Writing as usual $\bar{e} \equiv P(\vec{e})$, this relation may be reexpressed as

$$\bar{J}_{\vec{e}} = M^S(\bar{e}) + \vec{e}\cdot\vec{n}\,\bar{\Gamma} \tag{6.1}$$

where

$$M^S = PM_0P + \tilde{S}PM_1P + \mathrm{Grad}\, v^\perp \otimes \bar{a}_1 + \tilde{S}(\mathrm{Grad}\, v^\perp) \otimes \bar{a}_2 \tag{6.2}$$

and

$$\bar{\Gamma} = (PM_0 + \tilde{S}PM_1)(\vec{n}) + a_1^\perp \mathrm{Grad}\, v^\perp + a_2^\perp \tilde{S}(\mathrm{Grad}\, v^\perp) \tag{6.3}$$

with $\bar{a}_m \equiv P(\vec{a}_m)$ and $a_m^\perp \equiv \vec{n}\cdot\vec{a}_m$.

At each point $\vec{p}$ of Σ_t, the linear operators on the right-hand side of eq.(6.2) must of course be understood as restricted to $T_{\vec{p}}(\Sigma_t)$. From eqs.(3.3) and (6.1), it follows that the balance equation for $\vec{e}\cdot\vec{a}^S$ reads

$$\frac{d^\perp \vec{e}\cdot\vec{a}^S}{dt} - 2Hv^\perp \vec{e}\cdot\vec{a}_s + \mathrm{Div}[M^S(\bar{e}) + \vec{e}\cdot\vec{n}\,\bar{\Gamma}] - \vec{e}\cdot\vec{\sigma}_s + [\![\vec{n}\cdot M(\vec{e}) - \vec{e}\cdot\vec{a}\, v^\perp]\!] = 0 .$$

This equation is *formally* identical with eq.(2.29) so that the steps that led from the latter to eq.(2.31) may be repeated, yielding the vector surface balance equation in the general theory:

$$\frac{d^\perp \vec{a}_s}{dt} - 2Hv^\perp \vec{a}_s + \mathrm{Div}M^S + \overline{\mathrm{Tr}}(SM^S)\vec{n} + (\mathrm{Div}\,\bar{\Gamma})\vec{n} - S(\bar{\Gamma}) - \vec{\sigma}_s + [\![M^*(\vec{n}) - v^\perp \vec{a}]\!] = \vec{0} . \tag{6.4}$$

This is *formally* identical with eq.(2.31). One difference is naturally that we now have detailed interpretations for $\vec{a}_s$, $\vec{\sigma}_s$ and M^S and $\bar{\Gamma}$ (eqs.(6.2) and (6.3)).

CHAPTER IV

BALANCE EQUATIONS OF HIGHER NORMAL MOMENTS

In Chapter III, we obtained the first surface balance equation which was formally identical with that used in the empirical approach. This provided us with a detailed interpretation of the surface fields used in the empirical approach in terms of normal moments of the deviations. It is interesting to know that the higher order moments also obey exact balance equations of a similar nature, though not involving the bulk fields. It is the object of the present chapter to derive these equations and discuss the terms that enter them. Despite the fact that these equations, unlike the first surface balance equation, have no equivalent in the empirical approach, the first of them will provide us with an interpretation of the transversality condition (eq. (II.2.22)) in the context of the general theory. This will be discussed in Section 3.

1) Balance equations for individual normal moments

The goal of this section is to obtain balance equations for the normal moments a_m, $m \geq 1$, defined by eq.(III.2.9)

A cartesian frame *fixed in space* is introduced, whose origin coincides with a point of the dividing surface Σ_{t_0} at time

t_0 and whose z axis is parallel to the unit normal $\vec{n}_0$ at that point. From eqs.(III.2.10) and (III.2.8) we have, at time t_0, with $m \geq 1$,

$$j^{\perp}_{m-1}(\vec{0}) = \vec{n}_0 \cdot \vec{J}_{m-1}(\vec{0}) = \int_{-\infty}^{\infty} z^{m-1} J^{\perp}_3(z\vec{n}_0, t_0)\, dz$$

$$= -\frac{1}{m} \int_{-\infty}^{\infty} z^m \frac{\partial J^{\perp}_3}{\partial z}(z\vec{n}_0, t_0)\, dz = -\frac{1}{m} \left\langle \frac{\partial J^{\perp}_3}{\partial z} \right\rangle_m (\vec{0}) \quad .$$

The limits of integration have been pushed to infinity in view of later simplifications in the notations. The jump in $J^{\perp}_3$ at $\vec{0}$ makes no contribution in the integration by parts, thanks to the factor z^m $(m \geq 1)$. Finally the fact that $\frac{\partial J^{\perp}_3}{\partial z}$ is not defined at $\vec{0}$ is obviously irrelevant. With the help of eq.(III.2.3),the last equation may be rewritten as

$$m j^{\perp}_{m-1} = -\sigma_m + \left\langle \frac{\partial a'}{\partial t} \right\rangle_m + \left\langle \frac{\partial J^{\perp}_1}{\partial x} + \frac{\partial J^{\perp}_2}{\partial y} \right\rangle_m \qquad (1.1)$$

We first concentrate on $\left\langle \frac{\partial a'}{\partial t} \right\rangle_m$. To bring out the moment a_m, we write

$$\left\langle \frac{\partial a'}{\partial t} \right\rangle_m = \int_{-\infty}^{\infty} z^m \frac{\partial a'}{\partial t}(z\vec{n}_0, t_0)\, dz = \frac{d}{dt} \int_{-\infty}^{\infty} z^m a'(z\vec{n}_0, t)\, dz \Big|_{t=t_0} . \qquad (1.2)$$

Here again thanks to the factor z^m, the jump in a' makes no contribution. At time t the dividing surface cuts the z axis at $z = Z(t)$; in particular $Z(t_0) = 0$. With $\vec{Q}(t)$ defined by $\vec{Q}(t) = Z(t)\vec{n}_0$, it is easy to see that $\dot{\vec{Q}}(t_0) = v^{\perp}\vec{n}_0$, where $v^{\perp}$ is the normal velocity of Σ_{t_0} at $\vec{0}$. The difference $\vec{n}_0 - \vec{n}(\vec{Q}(t))$ will be denoted by $\Delta\vec{n}(t)$. After making the change of variable $z = Z(t) + \zeta$

in the last integral, we get

$$\int_{-\infty}^{\infty} z^m a'(z\vec{n}_0,t)\,dz = \sum_{\kappa=0}^{m} \frac{m!}{(m-\kappa)!\kappa!} Z^\kappa \int_{-\infty}^{\infty} \zeta^{m-\kappa} a'[(Z+\zeta)\vec{n}_0,t]\,d\zeta$$

which on account of $Z(t_0) = 0$ and $\dot{Z}(t_0) = v^\perp$, gives

$$\frac{d}{dt}\int_{-\infty}^{\infty} z^m a'(z\vec{n}_0,t)\,dz\,\Big|_{t=t_0} = mv^\perp a_{m-1} + \frac{d}{dt}\int_{-\infty}^{\infty} \zeta^m a'[(Z+\zeta)\vec{n}_0,t]\,d\zeta\,\Big|_{t=t_0} . \tag{1.3}$$

Now at any point $\vec{q}$ not on Σ_t we may write

$$a'(\vec{q}+\vec{h},t) = a'(\vec{q},t) + \vec{h}\cdot\nabla a'(\vec{q},t) + |\vec{h}|^2 R(\vec{q},t;\vec{h})$$

where the function R is bounded on any bounded domain of variation of its arguments. Applying this to the integrand in eq.(1.3) gives

$$\int_{-\infty}^{\infty} \zeta^m a'[(Z+\zeta)\vec{n}_0,t]\,d\zeta = \int_{-\infty}^{\infty} \zeta^m a'[Z\vec{n}_0+\zeta\vec{n}+\zeta\Delta\vec{n},t]\,d\zeta$$

$$= \int_{-\infty}^{\infty} \zeta^m \{a'(Z\vec{n}_0+\zeta\vec{n},t)+\zeta\Delta\vec{n}\cdot\nabla a'(Z\vec{n}_0+\zeta\vec{n},t)+|\zeta\Delta\vec{n}|^2 R(Z\vec{n}_0+\zeta\vec{n},t;\zeta\Delta\vec{n})\}\,d\zeta$$

$$= a_m(\vec{Q}(t)) + \Delta\vec{n}(t)\cdot[\langle\nabla a'\rangle_{m+1}(\vec{Q}(t))] + |\Delta\vec{n}(t)|^2\int_{-\infty}^{\infty} \zeta^{m+2} R(Z\vec{n}_0+\zeta\vec{n},t;\zeta\Delta\vec{n})\,d\zeta . \tag{1.4}$$

But from eq.(II.1.19). it follows that $\frac{d}{dt} a_m\circ\vec{Q}(t_0) = \frac{d^\perp}{dt} a_m(\vec{0},t_0)$ while, from eq.(II.1.26), $\frac{d}{dt}\Delta\vec{n}(t_0) = \mathrm{Grad}\, v^\perp(\vec{0})$, and finally the time derivative of the last term in eq.(1.4) vanishes at t_0 since on account of $|\Delta\vec{n}|^2 = 2[1 - \vec{n}_0\cdot\vec{n}(\vec{Q})]$, both $|\Delta\vec{n}|^2$ and its time derivative vanish at t_0. There results the following expression for $\langle\frac{\partial a'}{\partial t}\rangle_m$:

$$\langle\frac{\partial a'}{\partial t}\rangle_m = \frac{d^\perp a}{dt}_m + mv^\perp a_{m-1} + \mathrm{Grad}\, v^\perp\cdot\langle\nabla a'\rangle_{m+1} \quad (m\geq 1) . \tag{1.5}$$

The last term in eq.(1.1) will now be rewritten in a manifestly invariant form. From the definition of the directional derivative, it follows that for any $\bar{u} \in T_{\vec{p}}(\Sigma_t)$

$$D_{\bar{u}}\langle\vec{J}'\rangle_m(\vec{p}) = \frac{d}{d\xi}\int_{-\infty}^{\infty}\zeta^m\vec{J}'[\vec{C}(\xi)+\zeta\vec{n}(\vec{C}(\xi))]\,d\zeta\,\Big|_{\xi=0}$$

where $\vec{C}$ is any curve in Σ_t such that $\vec{C}(0) = \vec{p}$ and $\frac{d\vec{C}}{d\xi}(0) = \bar{u}$. The right-hand side may be rewritten as

$$\int_{-\infty}^{\infty}\zeta^m[D_{\bar{u}-\zeta S(\bar{u})}\vec{J}'](\vec{p}+\zeta\vec{n}(\vec{p}))\,d\zeta = \langle D_{\bar{u}}\vec{J}'\rangle_m - \langle D_{S(\bar{u})}\vec{J}'\rangle_{m+1}$$

so that

$$\langle D_{\bar{u}}\vec{J}'\rangle_m = D_{\bar{u}}\langle\vec{J}'\rangle_m + \langle D_{S(\bar{u})}\vec{J}'\rangle_{m+1} \quad . \tag{1.6}$$

Introducing the covariant derivative $\bar{\nabla}\bar{J}_m$ defined by eq.(II.1.4) and using eqs.(III.2.10) and (II.1.14), the first term on the right may be rewritten as

$$D_{\bar{u}}\langle\vec{J}'\rangle_m = [\bar{\nabla}\bar{J}_m - j_m^{\perp}S](\bar{u}) + [\bar{u}\cdot(S(\bar{J}_m)+\mathrm{Grad}\,j_m^{\perp})]\,\vec{n} \quad . \tag{1.7}$$

Introducing likewise the covariant derivative $(D\vec{J}')_{\vec{q}}$ which, for each fixed $\vec{q}$ not on Σ_t, is a linear operator on $\mathbb{R}^3$ defined by $(D\vec{J}')_{\vec{q}}(\vec{h}) = D_{\vec{h}}\vec{J}'(\vec{q})$, the second term in eq.(1.6) may be rewritten as

$$\langle D_{S(\bar{u})}\vec{J}'\rangle_{m+1} = \langle(D\vec{J}')S\rangle_{m+1}(\bar{u}) \quad .$$

It follows that

$$\langle\frac{\partial J_1'}{\partial x} + \frac{\partial J_2'}{\partial y}\rangle_m = \mathrm{Div}\,\bar{j}_m - 2Hj_m^{\perp} + \overline{\mathrm{Tr}}\langle P(D\vec{J}')S\rangle_{m+1} \quad ,$$

where use has been made of eq.(II.1.13) and where P is the pro-

jector on $T_{\vec{p}}(\Sigma_{t_0})$.

Combining this equation with eqs.(1.1) and (1.5) finally yields the requisite balance equation

$$\frac{d^{\perp}a}{dt}_m - 2Hj^{\perp}_m + \mathrm{Div}\,\vec{j}_m - \sigma_m + m(a_{m-1}v^{\perp} - j^{\perp}_{m-1}) + \mathrm{Grad}\,v^{\perp}\cdot\langle\nabla a'\rangle_{m+1} + \overline{\mathrm{Tr}}\langle P(D\vec{J}')S\rangle_{m+1} = 0 \qquad (1.8)$$

which, needless to say, applies only when $m \geq 1$. Some comments about the last two terms are in order. Clearly, the fact that $\nabla a'$ and $D\vec{J}'$ are not defined on the dividing surface is irrelevant in computing the moments. (Derivatives are *not* meant in the sense of distribution theory.) Next we shall consider the size of these terms. The first one may be rewritten as

$$\mathrm{Grad}\,v^{\perp}\cdot\langle\nabla a'\rangle_{m+1} = \mathrm{Grad}\,v^{\perp}\cdot P(\langle\nabla a'\rangle_{m+1}) = \mathrm{Grad}\,v^{\perp}\cdot\langle P(\nabla a')\rangle_{m+1} .$$

Whence this scalar product actually involves only the tangential part of $\langle\nabla a'\rangle_{m+1}$. Because variations of the deviations along surfaces parallel to Σ_t are comparatively slow, it follows that $\mathrm{Grad}\,v^{\perp}\cdot\langle\nabla a'\rangle_{m+1}$ should be small compared to the other terms of order m-1 and m appearing in eq.(1.8). This would clearly not have been the case, had the normal component of $\langle\nabla a'\rangle_{m+1}$ been involved. Likewise, the term $\overline{\mathrm{Tr}}\langle P(D\vec{J}')S\rangle_{m+1}$ ought to be small compared to terms of order m-1 and m, thanks to the factor S which insures that only tangential derivatives of $\vec{J}'$ are picked up.

An apparent drawback of eq.(1.8) is that the last two

terms involve quantities which are not expressed in terms of the normal moments used hitherto (the a_k's, $\bar{j}_k$'s and $j_k^{\perp}$'s). This can be largely remedied with the help of convenient recurrence relations that will be derived presently. By an argument identical to the one which led to eq.(1.6), it follows that for any $\bar{u} \in T_{\vec{p}}(\Sigma_t)$

$$\bar{u}\cdot\langle\nabla a'\rangle_k = \bar{u}\cdot\mathrm{Grad}\, a_k + S(\bar{u})\cdot\langle\nabla a'\rangle_{k+1}$$

$$= \bar{u}\cdot\mathrm{Grad}\, a_k + \bar{u}\cdot SP(\langle\nabla a'\rangle_{k+1})$$

which, since $\bar{u}$ is an arbitrary vector in $T_{\vec{p}}(\Sigma_t)$, implies that

$$P(\langle\nabla a'\rangle_k) = \mathrm{Grad}\, a_k + SP(\langle\nabla a'\rangle_{k+1}) \ . \qquad (1.9)$$

The length of the second vector on the right-hand side will be roughly of the order of δ/R times that of the first, where $1/R$ is the largest normal curvature of Σ_t at the point where these vectors are evaluated. Under usual physical conditions, R is enormously greater than δ so that the second vector may be safely neglected. Hence coming back to eq.(1.8), we may write

$$\mathrm{Grad}\, v^{\perp}\cdot\langle\nabla a'\rangle_{m+1} \simeq \mathrm{Grad}\, v^{\perp}\cdot \mathrm{Grad}\, a_{m+1}$$

with a high degree of precision. Should that not prove good enough, for instance if it were necessary to consider normal moments of several orders at the same time, a more refined approximation could be obtained by noting that for any integer $r \geq 1$

$$P(\langle\nabla a'\rangle_k) = \mathrm{Grad}\, a_k + S(\mathrm{Grad}\, a_{k+1}) + \ldots + S^r(\mathrm{Grad}\, a_{k+r}) + S^{r+1}P(\langle\nabla a'\rangle_{k+r+1}) \ . \qquad (1.10)$$

This relation follows by iterating eq.(1.9). In fact it is obvious that the last term goes to $\vec{0}$ as r goes to ∞ so that eq.(1.10) gen-

erates a series converging to $P(\langle \nabla a' \rangle_k)$:

$$P(\langle \nabla a' \rangle_k) = \sum_{r=0}^{\infty} S^r \mathrm{Grad}\, a_{k+r} \quad . \tag{1.11}$$

But under usual physical conditions this series will converge so rapidly that the first term will already be an excellent approximation. In any case, eq.(1.10) provides an explicit expression of the remainder at any order of truncation.

A similar recurrence relation can be derived for $\langle P(D\vec{J}')S \rangle_k$. From eqs.(1.6) and (1.7), it follows that for any $\bar{u} \in T_{\vec{p}}(\Sigma_t)$,

$$\langle P(D\vec{J}')P \rangle_k(\bar{u}) = P(\langle D_{\bar{u}} \vec{J}' \rangle_k)$$

$$= (\bar{\nabla} \bar{J}_k - j_k^{\perp} S)(\bar{u}) + \langle P(D\vec{J}')S \rangle_{k+1}(\bar{u})$$

from which

$$\langle P(D\vec{J}')P \rangle_k = \bar{\nabla} \bar{J}_k - j_k^{\perp} S + \langle P(D\vec{J}')S \rangle_{k+1} \quad . \tag{1.12}$$

Multiplying on the right side by S gives the requisite recurrence relation

$$\langle P(D\vec{J}')S \rangle_k = (\bar{\nabla} \bar{J}_k - j_k^{\perp} S)S + \langle P(D\vec{J}')S \rangle_{k+1} S \quad . \tag{1.13}$$

Upon writing $\Omega_k \equiv \bar{\nabla} \bar{J}_k - j_k^{\perp} S$, it follows that for any integer $r \geq 1$

$$\langle P(D\vec{J}')S \rangle_k = \Omega_k S + \ldots + \Omega_{k+r} S^{r+1} + \langle P(D\vec{J}')S^{r+2} \rangle_{k+r+1} . \tag{1.14}$$

The comments that were made about the next to last term in eq.(1.8) apply verbatim to the last term $\overline{Tr}\langle P(D\vec{J}')S \rangle_{m+1}$. Thus form eq.(1.14) we have, with a high degree of precision

$$\overline{Tr}\langle P(D\vec{J}')S \rangle_k \simeq \overline{Tr}(\Omega_k S) = \overline{Tr}(S\bar{\nabla} \bar{J}_k) - j_k^{\perp} \overline{Tr}(S^2)$$

$$= \overline{\mathrm{Tr}}[(\tilde{S} + 2HI)\overline{\nabla}\bar{j}_k] - j_k^{\perp}(4H^2 - 2K)$$

$$= \overline{\mathrm{Tr}}[\tilde{S}\overline{\nabla}\bar{j}_k] + 2H\mathrm{Div}\,\bar{j}_k + j_k^{\perp}(2K-4H^2)$$

$$= \mathrm{Div}\,\tilde{S}(\bar{j}_k) + 2H\mathrm{Div}\,\bar{j}_k + j_k^{\perp}(2K-4H^2)$$

where in the last step we have used eq.(II.1.9) together with the identity $\mathrm{Div}\,\tilde{S} = 0$, which is equivalent to

$$\mathrm{Div}\,S = 2\,\mathrm{Grad}\,H\,. \qquad (1.15)$$

The proof of this equation will be given in the next section. Better approximations could be obtained if necessary from eq.(1.14). The procedure for obtaining balance equations for normal moments of any order is now clear: one starts with the basic relation expressed by eq.(1.8) and uses eqs.(1.10) and (1.14) to reexpress the last two terms in eq.(1.8) if necessary. One thereby obtains a hierarchy whose truncation can be based on clear physical arguments.

2) Balance equations for combined normal moments

The balance equations derived in the previous section (eq.(1.8)) involved terms (the last two) which were not expressed directly in terms of the moments used up to that point (a_k, $\bar{j}_k$ and $j_k^{\perp}$). We showed how this could be remedied at the expense of very mild approximations. In this section we shall see that the balance equations for the normal moments of order ≥ 1 can be combined three at a time to obtain exact equations very similar to the first surface balance equation of Chapter III, and involving only moments

of the type a_k, $\bar{j}_k$ and $j_k^\perp$.

From eq. (1.11) together with $-2HI = -S + \tilde{S}$ and $\tilde{S}S = S\tilde{S} = -KI$ (see eqs.(III.2.20) and (III.2.22)), we have

$$P(<\nabla a'> - 2H<\nabla a'>_{k+1} + K<\nabla a'>_{k+2})$$

$$= \sum_{r=0}^{\infty} S^r(\mathrm{Grad}\, a_{k+r}) - \sum_{r=0}^{\infty} S^{r+1}(\mathrm{Grad}\, a_{k+r+1})$$

$$+ \sum_{r=0}^{\infty} \tilde{S}S^r(\mathrm{Grad}\, a_{k+r+1}) - \sum_{r=0}^{\infty} \tilde{S}\, S^{r+1}(\mathrm{Grad}\, a_{k+r+2})$$

$$= \mathrm{Grad}\, a_k + \tilde{S}(\mathrm{Grad}\, a_{k+1}) \,. \qquad (2.1)$$

Likewise with

$$M_k \equiv <P(D\vec{J}')S>_k - 2H<P(D\vec{J}')S>_{k+1} + K<P(D\vec{J}')S>_{k+2} \qquad (2.2)$$

we have, using eq.(1.14),

$$M_k = \sum_{r=0}^{\infty} \Omega_{k+r} S^{r+1} - \sum_{r=0}^{\infty} \Omega_{k+r+1} S^{r+2} + \sum_{r=0}^{\infty} \Omega_{k+r+1} S^{r+1}\tilde{S} - \sum_{r=0}^{\infty} \Omega_{k+r+2} S^{r+2}\tilde{S}$$

$$= \Omega_k S + \Omega_{k+1} S\tilde{S} = \Omega_k S - K\Omega_{k+1} \,. \qquad (2.3)$$

We calculated $\overline{\mathrm{Tr}}(\Omega_k S)$ at the end of the previous section, and $\overline{\mathrm{Tr}}(\Omega_{k+1}) = \overline{\mathrm{Tr}}(\bar{\nabla}\bar{j}_{k+1} - j_{k+1}^\perp S) = \mathrm{Div}\,\bar{j}_{k+1} - 2Hj_{k+1}^\perp$. Combining these results we find that

$$\overline{\mathrm{Tr}}M_k = \mathrm{Div}[\tilde{S}(\bar{j}_k)] + 2H\mathrm{Div}\,\bar{j}_k - K\mathrm{Div}\,\bar{j}_{k+1}$$
$$+ (2K - 4H^2)j_k^\perp + 2HKj_{k+1}^\perp \,. \qquad (2.4)$$

Let us define the following combined moments in terms of the normal moments defined by eqs.(III.2.9,10) :

$$a_m^S \equiv a_m - 2Ha_{m+1} + Ka_{m+2}$$
$$\sigma_m^S \equiv \sigma_m - 2H\sigma_{m+1} + K\sigma_{m+2} \qquad (2.5)$$
$$j_m^{\perp S} \equiv j_m^\perp - 2Hj_{m+1}^\perp + Kj_{m+2}^\perp \,.$$

When $m = 0$, these are the surface excess densities (see eqs. (III.2.11,12)). We now pick three of the balance equations (eq.(1.8)) of order $m, m+1, m+2$ ($m \geq 1$), multiply the second one by -2H and the third one by K and add up all three to get (using eqs.(2.1) and (2.2))

$$\frac{d^{\perp}a_m^s}{dt} - 2Hj_m^{\perp s} + 2a_{m+1}\frac{d^{\perp}H}{dt} - a_{m+2}\frac{d^{\perp}K}{dt} + \mathrm{Div}\,\bar{j}_m - 2H\mathrm{Div}\,\bar{j}_{m+1}$$
$$+ K\mathrm{Div}\,\bar{j}_{m+2} - \sigma_m^s + m(a_{m-1}v^{\perp} - j_{m-1}^{\perp}) - 2H(m+1)(a_m v^{\perp} - j_m^{\perp})$$
$$+ K(m+2)(a_{m+1}v^{\perp} - j_{m+1}^{\perp}) + \mathrm{Grad}\,v^{\perp}\cdot[\mathrm{Grad}\,a_{m+1} + \tilde{S}(\mathrm{Grad}\,a_{m+2})] + \overline{\mathrm{Tr}\,M}_{m+1} = 0 \qquad (2.6)$$

Now we shall show at the end of this section that

$$\frac{d^{\perp}H}{dt} = (2H^2 - K)v^{\perp} + \tfrac{1}{2}\mathrm{Lap}\,v^{\perp} \qquad (\mathrm{Lap}\,v^{\perp} \equiv \mathrm{Div}\,\mathrm{Grad}\,v^{\perp}) \quad (2.7)$$

and

$$\frac{d^{\perp}K}{dt} = 2HKv^{\perp} - \mathrm{Div}[\tilde{S}(\mathrm{Grad}\,v^{\perp})]\,. \qquad (2.8)$$

Using the self-adjointness of $\tilde{S}$, we have

$$\mathrm{Grad}\,v^{\perp}\cdot[\mathrm{Grad}\,a_{m+1} + \tilde{S}(\mathrm{Grad}\,a_{m+2})] = \mathrm{Div}\,(a_{m+1}\mathrm{Grad}\,v^{\perp}) - a_{m+1}\mathrm{Lap}\,v^{\perp}$$
$$+ \mathrm{Div}[a_{m+2}\tilde{S}(\mathrm{Grad}\,v^{\perp})] - a_{m+2}\mathrm{Div}[\tilde{S}(\mathrm{Grad}\,v^{\perp})]\,.$$

Inserting this together with eqs.(2.4), (2.7) and (2.8) into eq.(2.6), the latter reduces to

$$\frac{d^{\perp}a_m^s}{dt} - 2Hv^{\perp}a_m^s + \mathrm{Div}[\bar{j}_m + \tilde{S}(\bar{j}_{m+1}) + a_{m+1}\mathrm{Grad}\,v^{\perp} + a_{m+2}\tilde{S}(\mathrm{Grad}\,v^{\perp})]$$
$$- \sigma_m^s + m(a_{m-1}^s v^{\perp} - j_{m-1}^{\perp s}) = 0 \qquad (2.9)$$
$$(m \geq 1)\,.$$

This equation is exact and has a remarkable similarity of struc-

ture with the first surface balance equation, eq.(III.3.3). This suggests that the same technique could be used to derive the first surface balance equation. Indeed, eq.(1.8) may be shown to hold also for $m = 0$ provided that the term $m(a_{m-1}v^{\perp} - j^{\perp}_{m-1})$ be replaced by $-[\![\vec{J}'\cdot\vec{n} - a'v^{\perp}]\!] = [\![\vec{J}\cdot\vec{n} - av^{\perp}]\!]$, and the same calculations as above may be repeated, leading eventually to eq.(III.3.3). But this procedure would only establish the first surface balance equation as a *necessary* condition for the formal balance equation (eq.(III.3.1)) to hold, whereas the derivation given in Chapter III shows clearly that it is both a necessary and *sufficient* condition.

We will now give the proofs of eqs.(2.7) and (2.8) and next of eq.(1.15), which were used in deriving eq. (2.9). We take Σ_t at a fixed time t as a reference configuration. If $\bar{u}_1, \bar{u}_2$ are two tangent vector fields, linearly independent on each tangent plane, we have

$$2H = \bar{u}_1^* \cdot S(\bar{u}_1) + \bar{u}_2^* \cdot S(\bar{u}_2) \tag{2.10}$$

and
$$K = [\bar{u}_1^* \cdot S(\bar{u}_1)][\bar{u}_2^* \cdot S(\bar{u}_2)] - [\bar{u}_1^* \cdot S(\bar{u}_1)][\bar{u}_2^* \cdot S(\bar{u}_2)] \tag{2.11}$$

where $(\bar{u}_1^*, \bar{u}_2^*)$ is the basis reciprocal to $(\bar{u}_1, \bar{u}_2)$, that is $\bar{u}_\alpha^* \cdot \bar{u}_\beta^* = \delta_{\alpha\beta}$, so that

$$\bar{u}_1^* = \frac{\bar{u}_2 \times \vec{n}}{\Omega} \qquad \bar{u}_2^* = \frac{\vec{n} \times \bar{u}_1}{\Omega} \tag{2.12}$$

where $\Omega = \vec{n}\cdot(\bar{u}_1 \times \bar{u}_2)$. Now we let $\bar{u}_1$ and $\bar{u}_2$ be "normally convected" on $\Sigma_{t+\tau}$ according to the definition of Section 1 of Chapter II. It is then a simple matter to show that

$$\frac{d^{\perp}}{dt} S(\bar{u}_\alpha)\Big|_{\tau=0} = \bar{\nabla}_{\bar{u}_\alpha} \operatorname{Grad} v^{\perp} + S(\bar{u}_\alpha)\cdot \operatorname{Grad} v^{\perp}\vec{n}$$

while from eqs (II.1.24) and (II.1.25)

$$\frac{d^{\perp}\bar{u}_{\alpha}}{d\tau}\bigg|_{\tau=0} = - v^{\perp}S(\bar{u}_{\alpha}) + \bar{u}_{\alpha}\cdot \mathrm{Grad}\, v^{\perp}\vec{n}$$

and

$$\frac{d^{\perp}\Omega}{d\tau}\bigg|_{\tau=0} = - 2Hv^{\perp} .$$

Combining these results with the normal time derivatives of eqs. (2.10,11) and doing some algebra, we get eqs.(2.7) and (2.8). The calculation is much simplified if $\bar{u}_1$, $\bar{u}_2$ are chosen to be eigenvectors of S on the reference configuration Σ_t, which is always possible.

We now come to eq.(1.15). Although it looks very simple, its proof is not so straightforward. The formula is likely to be known to some differential geometers, but we could not trace it in any of the several standard references we looked through. The crucial ingredient in the proof is the Codazzi-Mainardi identity. Let $\vec{p}$ be a point of a surface Σ and $\bar{u}_1$, $\bar{u}_2$ be two orthogonal unit tangent vector fields defined on a neighborhood of $\vec{p}$ in Σ with $\bar{u}_2 = \vec{n}\times\bar{u}_1$. From eq.(II.1.8), we have

$$\bar{u}_1\cdot \mathrm{Div}S = \bar{u}_1\cdot[(\bar{\nabla}_{\bar{u}_1}S)(\bar{u}_1) + (\bar{\nabla}_{\bar{u}_2}S)(\bar{u}_2)] . \qquad (2.13)$$

The first term on the right may be developed as follows:

$$\begin{aligned}
\bar{u}_1\cdot(\bar{\nabla}_{\bar{u}_1}S)(\bar{u}_1) &= \bar{u}_1\cdot\bar{\nabla}_{\bar{u}_1}[S(\bar{u}_1)] - \bar{u}_1\cdot S(\bar{\nabla}_{\bar{u}_1}\bar{u}_1) \\
&= \bar{\nabla}_{\bar{u}_1}[\bar{u}_1\cdot S(\bar{u}_1)] - 2S(\bar{u}_1)\cdot\bar{\nabla}_{\bar{u}_1}\bar{u}_1 \\
&= \bar{u}_1\cdot\mathrm{Grad}\,2H - \bar{\nabla}_{\bar{u}_1}[\bar{u}_2\cdot S(\bar{u}_2)] - 2S(\bar{u}_1)\cdot\bar{\nabla}_{\bar{u}_1}\bar{u}_1 \\
&= \bar{u}_1\cdot\mathrm{Grad}\,2H - S(\bar{u}_2)\cdot\bar{\nabla}_{\bar{u}_1}\bar{u}_2 - \bar{u}_2\cdot\bar{\nabla}_{\bar{u}_1}[S(\bar{u}_2)] \\
&\qquad - 2S(\bar{u}_1)\cdot\bar{\nabla}_{\bar{u}_1}\bar{u}_1
\end{aligned}$$

$$= \bar{u}_1 \cdot \mathrm{Grad}\, 2H - \bar{u}_2 \cdot \bar{\nabla}_{\bar{u}_2}[S(\bar{u}_1)]$$

$$- S(\bar{u}_2) \cdot (\bar{\nabla}_{\bar{u}_1} \bar{u}_2 + [\bar{u}_1, \bar{u}_2]) - 2 S(\bar{u}_1) \cdot \bar{\nabla}_{\bar{u}_1} \bar{u}_1 . \qquad (2.14)$$

In the last step, use has been made of the Codazzi-Mainardi equation

$$\bar{\nabla}_{\bar{X}} S(\bar{Y}) - \bar{\nabla}_{\bar{Y}} S(\bar{X}) = S([\bar{X}, \bar{Y}])$$

where $[\bar{X}, \bar{Y}]$ is the Lie bracket of the tangent vector fields $\bar{X}$ and $\bar{Y}$ (Hicks [1965], p.8,28). The second term in eq.(2.13) may be rewritten

$$\bar{u}_1 \cdot (\bar{\nabla}_{\bar{u}_2} S)(\bar{u}_2) = \bar{u}_1 \cdot \{\bar{\nabla}_{\bar{u}_2}[S(\bar{u}_2)] - S(\bar{\nabla}_{\bar{u}_2} \bar{u}_2)\}$$

$$= \bar{\nabla}_{\bar{u}_2}[\bar{u}_1 \cdot S(\bar{u}_2)] - S(\bar{u}_2) \cdot \bar{\nabla}_{\bar{u}_2} \bar{u}_1$$

$$- \bar{\nabla}_{\bar{u}_2}[S(\bar{u}_1) \cdot \bar{u}_2] + \bar{u}_2 \cdot \bar{\nabla}_{\bar{u}_2}[S(\bar{u}_1)]$$

$$= \bar{u}_2 \cdot \bar{\nabla}_{\bar{u}_2}[S(\bar{u}_1)] - S(\bar{u}_2) \cdot \bar{\nabla}_{\bar{u}_2} \bar{u}_1$$

$$= \bar{u}_2 \cdot \bar{\nabla}_{\bar{u}_2}[S(\bar{u}_1)] - S(\bar{u}_2) \cdot (\bar{\nabla}_{\bar{u}_1} \bar{u}_2 + [\bar{u}_2, \bar{u}_1])$$

where in the last step, use has been made of the identity $\bar{\nabla}_{\bar{u}_1} \bar{u}_2 - \bar{\nabla}_{\bar{u}_2} \bar{u}_1 = [\bar{u}_1, \bar{u}_2]$ (Hicks [1965], p.26). Inserting this, together with eq.(2.14) in eq.(2.13) yields

$$\bar{u}_1 \cdot \mathrm{Div}\, S = \bar{u}_1 \cdot \mathrm{Grad}\, 2H - 2[S(\bar{u}_2) \cdot \bar{\nabla}_{\bar{u}_1} \bar{u}_2 + S(\bar{u}_1) \cdot \bar{\nabla}_{\bar{u}_1} \bar{u}_1] . \qquad (2.15)$$

We will now show that the expression inside the square brackets vanishes. Since $\bar{u}_2 = \vec{n} \times \bar{u}_1$, we have

$$\bar{\nabla}_{\bar{u}_1} \bar{u}_2 = P[D_{\bar{u}_1}(\vec{n} \times \bar{u}_1) = P[(D_{\bar{u}_1} \vec{n}) \times \bar{u}_1 + \vec{n} \times D_{\bar{u}_1} \bar{u}_1]$$

$$= \vec{n} \times \bar{\nabla}_{\bar{u}_1} \bar{u}_1$$

from which

$$S(\bar{u}_2) \cdot \bar{\nabla}_{\bar{u}_1} \bar{u}_2 = S(\bar{u}_2) \cdot (\vec{n} \times \bar{\nabla}_{\bar{u}_1} \bar{u}_1)$$

$$= - \bar{\nabla}_{\bar{u}_1} \bar{u}_1 \cdot [\vec{n} \times S(\bar{u}_2)]$$

and $$S(\bar{u}_2)\cdot\bar{\nabla}_{\bar{u}_1}\bar{u}_2 + S(\bar{u}_1)\cdot\bar{\nabla}_{\bar{u}_1}\bar{u}_1 = [-\vec{n}\times S(\bar{u}_2) + S(\bar{u}_1)]\cdot\bar{\nabla}_{\bar{u}_1}\bar{u}_1 \ .$$

But since $\bar{u}_1$ is everywhere a unit vector, it follows that $\bar{\nabla}_{\bar{u}_1}\bar{u}_1$ is perpendicular to $\bar{u}_1$, that is $\bar{\nabla}_{\bar{u}_1}\bar{u}_1 = \alpha\bar{u}_2$, and the last expression may be rewritten as

$$[-\vec{n}\times S(\bar{u}_2) + S(\bar{u}_1)]\cdot\alpha\bar{u}_2 = \alpha[(\vec{n}\times\bar{u}_2)\cdot S(\bar{u}_2) + S(\bar{u}_1)\cdot\bar{u}_2]$$

$$= \alpha[-\bar{u}_1\cdot S(\bar{u}_2) + S(\bar{u}_1)\cdot\bar{u}_2] = 0$$

from the self-adjointness of S. Equation (2.15) thus reduces to

$$\bar{u}_1\cdot \mathrm{Div}\, S = \bar{u}_1\cdot \mathrm{Grad}\, 2H \ .$$

The same relation obviously holds for $\bar{u}_2$, so that

$$\mathrm{Div}\ S = \mathrm{Grad}\, 2H \ .$$

3) Application to the transversality condition of the BAM theory

In the previous chapter, we have provided the bridge between most of the equations underlying the empirical approach (eqs.(II.2.19-24)) and the general theory based on deviations. Equation (II.2.24) was given a rigorous exact analogue whereas eqs.(II.2.19-21) (especially the last one) were recovered in the context of a zeroth order approximation. However one last gap remained to be filled, eq.(II.2.22) :

$$j^{\perp} = a^{S} v^{\perp} \ . \qquad (3.1)$$

What we found in Section 4 of Chapter III was that the zeroth order contribution in eq.(III.4.16) gave

$$\int_{\Delta_t(\partial V)} \vec{J}' \cdot \vec{N}\, dA \simeq \int_{L_t(\partial V)} (\bar{j}_0 \cdot \bar{\nu} + \tau j_0^{\perp})\, d\lambda \qquad (3.2)$$

This has the same structure as the line integral in eq.(II.2.21) except that in the general theory $j_0^{\perp}$ is, according to eqs. (III.2.9,10), given by

$$j_0^{\perp} = \vec{n} \cdot \langle \vec{J}' \rangle_0 = \vec{n} \cdot \vec{J}_0 \qquad (3.3)$$

and not by an analogue of eq.(3.1). Since eq.(3.2) was obtained in the context of the zeroth order approximation, we might expect that eqs.(3.1) and (3.3) could be reconciled within the same context. This is confirmed by the balance equations derived in Section 1. Indeed the balance equation for the first order normal moment obtained by setting m = 1 in eq.(1.8) reads

$$\frac{d^{\perp} a_1}{dt} - 2H j_1^{\perp} + \mathrm{Div}\, \bar{j}_1 - \sigma_1 + (a_0 v^{\perp} - j_0^{\perp}) + \mathrm{Grad}\, v^{\perp} \cdot \langle \nabla a' \rangle_2 + \overline{\mathrm{Tr}} \langle P(D\vec{J}')S \rangle_2 = 0 .$$

In the zeroth order approximation we neglect all moments of order ≥ 1 . The above equation then reduces to

$$j_0^{\perp} = a_0 v^{\perp} . \qquad (3.4)$$

Since in the zeroth order approximation the surface excess a^s is set equal to a_0 (see eq.(III.2.11)), we have reconciled eqs.(3.1) and (3.3). The whole set of equations (II.2.19-24) which expresses the structure of the empirical approach has thus been given a firm basis in the context of the general theory. Equation (3.4) agrees with the transversality condition derived in the theory of Bedeaux, Albano and Mazur, as may be found for example in (Vodák [1978], eq.(13)).

Having obtained exact balance equations in terms of normal moments, our main concern has been to interpret the empirical formalism in terms of normal moments of the deviations. This could be achieved in the zeroth order approximation. It is to be expected that higher order approximations could be used to handle situations where very high curvatures are present or where the interface is not so thin. Buff [1956] has thus studied curvature effects in equilibrium . The theory developed in this chapter and in Chapter III could provide the basis for such an investigation in non-equilibrium situations. However at this early stage, we restrict our attention to features present in the empirical framework described in Chapter II.

CHAPTER V

MOMENTUM AND ENERGY

1) Mass and momentum balance

Let us consider an n-component system without chemical reactions, with schematic (i.e. bulk) and surface excess mass densities $\rho^1,\ldots,\rho^n$ and $\rho_s^1,\ldots,\rho_s^n$. We recall from Chapter III that

$$\rho_s^\alpha = \rho_0^\alpha - 2H\rho_1^\alpha + K\rho_2^\alpha \tag{1.1}$$

with $\rho_m^\alpha \equiv \langle(\rho^\alpha)'\rangle_m$.

The associated current densities are denoted by $\vec{J}^1,\ldots,\vec{J}^n$ and $\bar{j}^1,\ldots,\bar{j}^n$ where

$$\bar{j}^\alpha = \bar{j}_0^\alpha + \tilde{S}(\bar{j}_1^\alpha) + \rho_1^\alpha \mathrm{Grad}\, v^\perp + \rho_2^\alpha \tilde{S}(\mathrm{Grad}\, v^\perp) \tag{1.2}$$

and $\bar{j}_m^\alpha \equiv P(\vec{J}_m^\alpha) \equiv P(\langle(\vec{J}^\alpha)'\rangle)_m$.

The total densities are

$$\rho = \sum_{\alpha=1}^{n} \rho_\alpha \quad , \quad \vec{G} = \sum_{\alpha=1}^{n} \vec{J}^\alpha \quad , \quad \rho_s = \sum_{\alpha=1}^{n} \rho_s^\alpha \quad , \text{ and } \bar{g} = \sum_{\alpha=1}^{n} \bar{j}^\alpha \ . \tag{1.3}$$

The general balance equation of Chapter III together with the usual bulk balance equation become

$$\frac{\partial \rho^\alpha}{\partial t} + \nabla\cdot\vec{J}^\alpha = 0 \tag{1.4}$$

$$\frac{d^\perp \rho_s^\alpha}{dt} - 2Hv^\perp\rho_s^\alpha + \mathrm{Div}\,\bar{j}^\alpha + [\![\vec{J}^\alpha\cdot\vec{n} - \rho^\alpha v^\perp]\!] = 0 \tag{1.5}$$

and, on summing over α,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \vec{G} = 0 \tag{1.6}$$

$$\frac{d^{\perp}}{dt}\rho_s - 2Hv^{\perp}\rho_s + \mathrm{Div}\,\bar{g} + [\![\vec{G}\cdot\vec{n} - \rho v^{\perp}]\!] = 0 \ . \tag{1.7}$$

Equation (1.5) lends itself to a simple intuitive interpretation. On rewriting the last term as $[\![\rho^{\alpha}(\vec{w}^{\alpha}\cdot\vec{n} - v^{\perp})]\!]$, we see that $-[\![\vec{J}^{\alpha}\cdot\vec{n} - \rho^{\alpha}v^{\perp}]\!]$ may be interpreted as the rate of transfer of constituant α into the interface from the + phase minus the rate of transfer of constituant α from the interface to the - phase. This, together with the lateral transfer within the interface embodied in $\mathrm{Div}\,\bar{j}^{\alpha}$, gives the net rate of change of local adsorption of constituant α. In the zeroth order approximation, only the first terms on the right-hand side of eqs.(1.1) and (1.2) are retained.

The bulk total mass current density $\vec{G}$ and the bulk momentum density are one and the same. If Π denotes the momentum flux density tensor (Landau and Lifshitz [1966]) and $\vec{F}$ the body force per unit volume, the bulk momentum balance equation reads

$$\frac{\partial \vec{G}}{\partial t} + \nabla \cdot \Pi - \vec{F} = \vec{0} \ . \tag{1.8}$$

As before we ignore the subtleties associated with diffusion: partial stress tensors, etc.(Kehlen and Baranowski [1977]). The momentum surface excess density $\vec{G}_s$ is

$$\vec{G}_s = \vec{G}_0 - 2H\vec{G}_1 + K\vec{G}_2 \tag{1.9}$$

where

$$\vec{G}_m = \langle \vec{G}' \rangle_m = \sum_{\alpha=1}^{n} \vec{J}_m^{\alpha} \ .$$

Note that its tangential part $P(\vec{G}_s)$ is *not* equal to the vector $\bar{g}$ of eq.(1.3). For on defining

$$\bar{g}_m \equiv \sum_{\alpha=1}^{n} \bar{j}_m^{\alpha} = P(\langle \vec{G}' \rangle_m) \tag{1.10}$$

we have from eqs.(1.2) and (1.3)

$$\bar{g} = \bar{g}_0 + \tilde{S}(\bar{g}_1) + \rho_1 \mathrm{Grad}\, v^{\perp} + \rho_2 \tilde{S}(\mathrm{Grad}\, v^{\perp}) \quad , \tag{1.11}$$

whereas, according to eq.(1.9),

$$P(\vec{G}_s) = \bar{g}_0 - 2H\bar{g}_1 + K\bar{g}_2 \quad . \tag{1.12}$$

This is in marked contrast with what we had in the empirical approach (eq.(II.3.9)). The difference disappears again in the zeroth order approximation for the right-hand sides of eqs.(1.11) and (1.12) then both reduce to $\bar{g}_0$.

Let us denote by Π_m the m^{th} order normal moment of the deviation Π' of the momentum flux density tensor:

$$\Pi_m \equiv \langle \Pi' \rangle_m$$

and write

$$g_m^{\perp} \equiv \vec{n} \cdot \langle \vec{G}' \rangle_m \quad .$$

Then it follows from eqs.(III.6.1-3) that the momentum surface balance equation is

$$\frac{d^{\perp}\vec{G}_s}{dt} - 2Hv^{\perp}\vec{G}_s + \mathrm{Div}\,\Pi^s + \overline{\mathrm{Tr}}(S\Pi^s)\vec{n} + (\mathrm{Div}\,\bar{\Gamma}_{\ell})\vec{n}$$

$$- S(\bar{\Gamma}_{\ell}) - \vec{f}_s + [\![\Pi^*(\vec{n}) - v^{\perp}\vec{G}]\!] = \vec{0} \tag{1.13}$$

where

$$\Pi^s = P\Pi_0 P + \tilde{S}P\Pi_1 P + \mathrm{Grad}\, v^{\perp} \circledast \bar{g}_1 + \tilde{S}(\mathrm{Grad}\, v^{\perp}) \circledast \bar{g}_2 \tag{1.14}$$

and

$$\bar{\Gamma}_{\ell} = (P\Pi_0 + \tilde{S}P\Pi_1)(\vec{n}) + g_1^{\perp}\mathrm{Grad}\, v^{\perp} + g_2^{\perp}\tilde{S}(\mathrm{Grad}\, v^{\perp}) \quad . \tag{1.15}$$

Equation (1.13) is *formally* identical with the abstract empirical momentum balance equation (II.3.11) provided that $\bar{g} + \rho^s v^{\perp} \vec{n}$ is written as $\vec{G}^s$ in the latter. But the analogy is not complete. First in the empirical approach, we had $\vec{G}^s = \bar{g} + \rho^s v^{\perp} \vec{n}$ (see eq.(II.3.9)) so that $P(\vec{G}^s)$ was equal to $\bar{g}$, or in other words the tangential component of the surface momentum density was equal to surface mass current density. Intuition based on experience with bulk densities would certainly suggest such an equality. However on comparing eqs. (1.11) and (1.12), we come to the conclusion that it does not hold in the present context. Not surprisingly intuition is vindicated in the zeroth order approximation because $P(\vec{G}^s)$ and $\bar{g}$ are then both equal to $\bar{g}_0$.

Secondly, it follows from the exact balance equation (IV.2.9) that in general $\vec{G}_s \cdot \vec{n}$ is not equal to $\rho_s v^{\perp}$, as was the case in the empirical theory (eq.(II.3.9)). Yet another difference is that the relation $\bar{\Gamma}_{\ell} = v^{\perp} \bar{g}$ obtained in the empirical approach on the basis of angular momentum balance does not hold in the general theory (compare eqs.(1.11) and (1.15)).

Now it will be recalled that the relations $\vec{n} \cdot \vec{G}^s = \rho^s v^{\perp}$ and $\bar{\Gamma}_{\ell} = v^{\perp} \bar{g}$ were essential in going from eq.(II.3.1) to eq. (II.3.31). Consequently the latter intuitively appealing form of momentum balance equation has no exact analogue in the general theory.

It will come as no surprise now that complete analogy is however restored in the zeroth order approximation. In this approximation, all normal moments of order ≥ 1 are neglected. The surface

excess mass density ρ_s^α is thus replaced by ρ_0^α while $\vec{j}^\alpha$ is replaced by $\vec{j}_0^\alpha$ (see eqs. (1.1) and (1.2)). Likewise eqs.(1.9),(1.14) and (1.15) are replaced by

$$\vec{G}_s = \vec{G}_0 \tag{1.16}$$

$$\Pi^s = P\Pi_0 P \tag{1.17}$$

$$\overline{\Gamma}_\ell = P\Pi_0(\vec{n}) \ . \tag{1.18}$$

In the zeroth order approximation, eq.(IV.1.8) also provides us with the general BAM transversality condition

$$j_0^\perp = a_0 v^\perp \tag{1.19}$$

which we will now put to work. Since $\vec{G}$ is the current density associated to ρ, this condition gives us

$$\vec{n}\cdot\vec{G}_0 = \rho_0 v^\perp \ . \tag{1.20}$$

Combining this with eqs.(1.16) and (1.10) we find that in the zeroth order approximation

$$\vec{G}_s = \vec{G}_0 = \bar{g}_0 + \rho_0 v^\perp \vec{n} \tag{1.21}$$

which is in agreement with eq.(II.3.9). We will now see that from the transversality condition and from eq.(1.18) we recover the relation $\overline{\Gamma}_\ell = v^\perp \bar{g}$ which was obtained on the basis of angular momentum balance in the empirical approach. Let $\vec{e}$ be a constant vector and consider the scalar density $\vec{e}\cdot\vec{G}$ with associated current density $\Pi(\vec{e})$. The corresponding surface density, in the zeroth order approximation, is $\vec{e}\cdot\vec{G}_0$, while the zeroth order normal moment associated to the current density $\Pi(\vec{e})$ is $\Pi_0(\vec{e}) = \langle\Pi'\rangle_0(\vec{e})$. The general transversality condition (eq.(1.19)), for these particular quantities, takes the form

$$\vec{n}\cdot\Pi_0(\vec{e}) = \vec{e}\cdot\vec{G}_0 v^{\perp} \ . \tag{1.22}$$

Now we shall assume that Π and Π_* are symmetric, so that so is Π_0, from which $\vec{n}\cdot\Pi_0(\vec{e}) = \vec{e}\cdot\Pi_0(\vec{n})$. Since $\vec{e}$ is arbitrary, it follows that

$$\Pi_0(\vec{n}) = v^{\perp}\vec{G}_0 \tag{1.23}$$

which, combined with eqs.(1.18) and (1.21) gives

$$\overline{\Gamma}_{\ell} = v^{\perp}\bar{g}_0 \ . \tag{1.24}$$

The balance of angular momentum is used here implicitly through the assumed symmetry of Π_0, which enables us to go from eq.(1.22) to eq.(1.23). Substituting the zeroth order expressions for $\vec{G}_s$ and $\overline{\Gamma}_{\ell}$ into eq.(1.13) gives the momentum balance equation in the zeroth order approximation :

$$\frac{d^{\perp}}{dt}(\bar{g}_0 + \rho_0 v^{\perp}\vec{n}) - 2Hv^{\perp}(\bar{g}_0 + \rho_0 v^{\perp}\vec{n}) + \mathrm{Div}\,\Pi^S + \overline{\mathrm{Tr}}(S\Pi^S)\vec{n}$$

$$+ \mathrm{Div}(v^{\perp}\bar{g}_0)\vec{n} - S(v^{\perp}\bar{g}_0) - \vec{f}_0 + [\![\Pi(\vec{n}) - v^{\perp}\vec{G}]\!] = \vec{0} \ .$$

We may now of course rewrite it as

$$\rho_0\frac{D\vec{V}}{Dt} = \mathrm{Div}\,T^S + \overline{\mathrm{Tr}}(ST^S)\vec{n} + \vec{f}_0 + [\![(T - \rho\vec{w}_{\pi}\otimes\vec{w}_{\pi})(\vec{n})]\!] \tag{1.25}$$

where

$$\begin{aligned} &\vec{V} = \bar{v} + v^{\perp}\vec{n} \ , \quad \rho_0\bar{v} \equiv \bar{g} \ , \\ &T^S = -\Pi^S + \rho_0\bar{v}\otimes\bar{v} \ , \\ &\vec{w}_{\pi}^{\pm} \equiv \vec{w}^{\pm} - \vec{V} \quad \text{on } \Sigma_t \end{aligned} \tag{1.26}$$

and $\frac{D}{Dt}$ is defined as previously in terms of $\vec{V}$.

The zeroth order expression for the surface stress tensor T^S follows from eqs.(1.26) and (1.17) :

$$\begin{aligned} T^S &= -\Pi^S + \rho_0\bar{v}\otimes\bar{v} \\ &= -P\Pi_0 P + \rho_0\bar{v}\otimes\bar{v} \end{aligned}$$

$$= - P[<(-T + \rho\vec{w}\otimes\vec{w})'>_0 P + \rho_0\bar{v}\otimes\bar{v}$$

or

$$T^S = PT_0P - <(\rho\vec{w}_{//}\otimes\vec{w}_{//})'>_0 + \rho_0\bar{v}\otimes\bar{v} \qquad (1.27)$$

where $\bar{v} \equiv P(\vec{w})$. The absence of any curvature term in this expression is a consequence of the zeroth order approximation (contrast with eq. (1.14)). Naturally at each point $\vec{p} \in \Sigma_t$, T^S is a linear operator on $T_{\vec{p}}(\Sigma_t)$, so that the terms on the right-hand side of eq.(1.27) (or for that matter of eqs.(1.14),(1.17) and (1.26)) actually stand for the restriction to $T_{\vec{p}}(\Sigma_t)$ of the corresponding linear operators. Our final expression for the surface stress tensor shows that it arises from excess forces (PT_0P) and from a rather peculiar kinetic term, to which we shall return when we take up the question of kinetic energy from where we had left it in Section 4 of Chapter II.

2) Relative velocity residuals

In this section, we return to the question of energy with which we had closed Chapter II. This quantity, as well as related ones which will be considered below, introduces some complications because of its nonlinearity in other quantities. For the first time we meet with expressions that, even in the zeroth order approximation, may be at variance with those used in the empirical approach. Interestingly enough,the quantities or relations involved are precisely those which we could not justify on the basis of general principles in our attempted deductive approach to the empirical for-

malism in Chapter II. Interesting too, is the fact that all the potential discrepancies can be reduced to terms having the same basic structure and intimately connected with the behavior of the velocity distribution in the transition zone. In view of the complexities involved, we restrict the discussion to the zeroth order approximation at the outset.

We start with the kinetic energy excess. The tangential surface velocity field is defined as before by $\bar{g}_0 = \rho_0 \bar{v}$ where $\bar{g}_0 = P(\vec{G}_0)$. Moreover, in the zeroth order approximation, the BAM transversality condition holds so that we may write $\vec{n}\cdot\vec{G}_0 = \rho_0 v^{\perp}$. We then define a non-tangential velocity field on Σ_t by the relation

$$\vec{V} = \bar{v} + v^{\perp}\vec{n} \ , \tag{2.1}$$

and extend it to the neighboring three-dimensional space by defining it as constant along the normal at each point of the dividing surface. Finally we define a relative velocity $\vec{w}_r$ in this region by

$$\vec{w}_r(\vec{p} + \zeta\vec{n}) = \vec{w}(\vec{p} + \zeta\vec{n}) - \vec{V}(\vec{p}) \quad , \quad \vec{p} \in \Sigma_t$$

or briefly

$$\vec{w}_r = \vec{w} - \vec{V} \ . \tag{2.2}$$

The velocity $\vec{w}$ is the bulk or "schematic" velocity. In terms of the exact velocity $\vec{w}^*$, we define another relative velocity

$$\vec{w}_r^* = \vec{w}^* - \vec{V} \tag{2.3}$$

and denote the deviation $\vec{w}_r^* - \vec{w}_r$ by $\vec{w}_r'$. We are now ready to start. From eqs.(2.2) and (2.3), it follows that

$$(\rho w_r^2)' = \rho^*(\vec{w}^* - \vec{V})^2 - \rho(\vec{w} - \vec{V})^2$$
$$= \rho^* w^{*2} - \rho w^2 + (\rho^* - \rho)V^2 - 2(\rho^*\vec{w}^* - \rho\vec{w})\cdot\vec{V}$$
$$= (\rho w^2)' + \rho' V^2 - 2(\rho\vec{w})'\cdot\vec{V} \quad .$$

Taking the zeroth order normal moment of both sides and denoting by κ_0 the zeroth order energy surface excess $<(\frac{\rho w^2}{2})'>_0$, we get

$$\kappa_0 \doteq \tfrac{1}{2}\rho_0 V^2 + \tfrac{1}{2}<(\rho w_r^2)'>_0 \quad . \tag{2.3}$$

Thus, on top of the expected $\frac{1}{2}\rho_0 V^2$, we find a residual term which can be either positive or negative. We note incidentally that the last two terms in the zeroth order expression for the surface stress tensor can be combined into an expression similar to the above residual. Using the same trick we write

$$(\rho\vec{w}_r \otimes \vec{w}_r)' = \rho^*(\vec{w}^* - \vec{V}) \otimes (\vec{w}^* - \vec{V}) - \rho(\vec{w} - \vec{V}) \otimes (\vec{w} - \vec{V})$$
$$= \rho^*\vec{w}^* \otimes \vec{w}^* - \rho\vec{w} \otimes \vec{w} - \rho^*\vec{w}^* \otimes \vec{V} + \rho\vec{w} \otimes \vec{V} - \vec{V} \otimes \rho^*\vec{w}^*$$
$$+ \vec{V} \otimes \rho\vec{w} + (\rho^* - \rho)\vec{V} \otimes \vec{V}$$
$$= (\rho\vec{w} \otimes \vec{w})' - (\vec{G}' \otimes \vec{V} + \vec{V} \otimes \vec{G}') + \rho'\vec{V} \otimes \vec{V}$$

from which

$$<(\rho\vec{w} \otimes \vec{w})'>_0 = \rho_0\vec{V} \otimes \vec{V} + <(\rho\vec{w}_r \otimes \vec{w}_r)'>_0 \quad . \tag{2.4}$$

Combining this with eq.(1.27) gives

$$T^s = PT_0P - <P(\rho\vec{w}_r \otimes \vec{w}_r)'P>_0 \quad . \tag{2.5}$$

Ignoring external fields for simplicity, the balance equations for the exact kinetic and internal energy densities are known to be

$$\frac{\partial}{\partial t}(\rho^* \frac{w^{*2}}{2}) + \nabla\cdot[\rho^* \frac{w^{*2}}{2}\vec{w}^* - T_*(\vec{w}^*)] + \mathrm{Tr}(T_*\nabla\vec{w}^*) = 0$$

and

$$\frac{\partial u^*}{\partial t} + \nabla\cdot[u^*\vec{w}^* + \vec{J}_q^*] - \mathrm{Tr}(T_*\nabla\vec{w}^*) = 0$$

where, as we recall, the notation T_* for exact T is used instead of T^* to avoid confusion with the adjoint of T. In the zeroth order approximation, the surface source term for internal energy is therefore given by

$$\langle \mathrm{Tr}[(T\nabla\vec{w})']\rangle_0 = \mathrm{Tr}[\langle (T\nabla\vec{w})'\rangle_0] \quad .$$

Let us see how this compares to the source term considered in Section 4 of Chapter II. Still using the same trick, we write

$$\begin{aligned}(T\nabla\vec{w}_{\mathcal{R}})' &= T^*\nabla(\vec{w}^* - \vec{V}) - T\nabla(\vec{w} - \vec{V}) \\ &= (T\nabla\vec{w})' - T'\nabla\vec{V}\end{aligned}$$

from which

$$\mathrm{Tr}[\langle (T\nabla\vec{w})'\rangle_0] = \mathrm{Tr}(\langle T'\nabla\vec{V}\rangle_0) + \mathrm{Tr}[\langle (T\nabla\vec{w}_{\mathcal{R}})'\rangle_0] \quad . \qquad (2.6)$$

In order to write the first term on the right-hand side in terms of known normal moments, we must find an explicit expression for $\nabla\vec{V}$. To this end we introduce a parametrization $\vec{r}(\xi^1,\xi^2)$ of Σ_t and extend it to a parametrization

$$\vec{R}(\xi^1,\xi^2,\zeta) = \vec{r}(\xi^1,\xi^2) + \zeta\vec{n}$$

of the neighboring three-dimensional space. The extension of $\vec{V}$ to that space is of course given by

$$\vec{V}(\xi^1,\xi^2,\zeta) = \vec{V}(\xi^1,\xi^2,0) \equiv \vec{V}_0(\xi^1,\xi^2)$$

so that $(\vec{n}\cdot\nabla)\vec{V} = \vec{0}$. Now restricting the discussion to one particular point $\vec{p}$ of Σ_t, we may choose the parametrization $\vec{r}(\xi^1,\xi^2)$ in such a way that, at a point $\vec{p}$, $\frac{\partial\vec{r}}{\partial\xi^\alpha}$ is a unit eigenvector $\vec{e}_\alpha$ of the shape operator $S_{\vec{p}}$. It then follows from eq.(II.1.10) that at point $\vec{p}$

$$\frac{\partial\vec{R}}{\partial\xi^\alpha} = \frac{\partial\vec{r}}{\partial\xi^\alpha} - \zeta S\left(\frac{\partial\vec{r}}{\partial\xi^\alpha}\right) = (1 - k_\alpha\zeta)\vec{e}_\alpha$$

where k_α is the principal curvature in direction $\vec{e}_\alpha$. Now we have on the one hand

$$\frac{\partial \vec{V}}{\partial \xi^\alpha}(\xi^1, \xi^2, \zeta) = \frac{\partial \vec{V}_0}{\partial \xi^\alpha}(\xi^1, \xi^2) = D_{\vec{e}_\alpha} \vec{V}_0$$

and on the other hand

$$\frac{\partial \vec{V}}{\partial \xi^\alpha} = \left(\frac{\partial \vec{R}}{\partial \xi^\alpha} \cdot \nabla\right) \vec{V}$$

$$= \nabla_{\frac{\partial \vec{R}}{\partial \xi^\alpha}} \vec{V} = \nabla_{(1 - k_\alpha \zeta)\vec{e}_\alpha} \vec{V}$$

$$= (\nabla \vec{V})(I - \zeta S)(\vec{e}_\alpha) \quad .$$

Comparing these two relations, we conclude that

$$(\nabla \vec{V})(I - \zeta S) = D\vec{V}_0$$

from which (since $(\vec{n}\cdot\nabla)\vec{V} \equiv (\nabla \vec{V})(\vec{n}) = \vec{0}$)

$$\nabla \vec{V} = (\nabla \vec{V})P = (D\vec{V}_0)(I - \zeta S)^{-1} P \, .$$

But using eqs.(II.1.10) and (II.1.14), it follows that if $\bar{u}$ is any vector in $T_{\vec{p}}(\Sigma_t)$

$$D_{\bar{u}} \vec{V}_0 = D_{\bar{u}}(\bar{v} + v^\perp \vec{n})$$

$$= \bar{\nabla}_{\bar{u}} \bar{v} - v^\perp S(\bar{u}) + [\bar{u}\cdot S(\bar{v}) + \bar{u}\cdot \mathrm{Grad}\, v^\perp]\vec{n}$$

so that finally

$$\nabla \vec{V} = \{(\bar{\nabla}\bar{v} - v^\perp S) + \vec{n} \otimes [S(\bar{v}) + \mathrm{Grad}\, v^\perp]\}(I - \zeta S)^{-1} P$$

where, as is easily checked,

$$(I - \zeta S)^{-1} = \frac{1}{\Lambda(\zeta)} [(1 - 2H\zeta)I + \zeta S]$$

with $\Lambda(\zeta) \equiv 1 - 2H\zeta + K\zeta^2$. The ζ dependence of $\nabla \vec{V}$ comes through the factor $(I - \zeta S)^{-1}$. To zeroth order in ζ, we then obtain

$$\mathrm{Tr}(\langle T' \nabla \vec{V} \rangle_0) = \mathrm{Tr}[T_0(\Omega + \vec{n} \otimes \bar{U})P] \qquad (2.7)$$

where

$$\Omega \equiv \bar{\nabla}\bar{v} - v^{\perp}S$$

and

$$\bar{U} \equiv S(\bar{v}) + \mathrm{Grad}\, v^{\perp} .$$

Now we have

$$\mathrm{Tr}(T_0 \Omega P) = \overline{\mathrm{Tr}}(PT_0P\Omega)$$

$$= \overline{\mathrm{Tr}}(T^S\Omega) + \overline{\mathrm{Tr}}(PWP\Omega) \qquad (2.8)$$

where

$$W \equiv \langle(\rho \vec{w}_n \otimes \vec{w}_n)'\rangle_0 \qquad (2.9)$$

and use has been made of eq.(2.5). From the zeroth order relation

$$\Pi_0(\vec{n}) = v^{\perp}\vec{G}_0$$

and from

$$\Pi_0 = \langle -T' + (\rho\vec{w}\otimes\vec{w})'\rangle_0 = -T_0 + \langle(\rho\vec{w}\otimes\vec{w})'\rangle_0$$

$$= -T_0 + \rho_0\vec{V}\otimes\vec{V} + W$$

we get

$$v^{\perp}\vec{G}_0 = -T_0(\vec{n}) + v^{\perp}\vec{G}_0 + W(\vec{n}),$$

that is

$$T_0(\vec{n}) = W(\vec{n}) . \qquad (2.10)$$

It follows that

$$\mathrm{Tr}(T_0\vec{n}\otimes\bar{U}P) = \mathrm{Tr}[(T_0(\vec{n})\otimes\bar{U})P]$$

$$= \mathrm{Tr}[(PT_0(\vec{n}))\otimes\bar{U}]$$

$$= PW(\vec{n})\cdot\bar{U} = \bar{U}\cdot W(\vec{n})$$

$$= [S(\bar{v}) + \mathrm{Grad}\, v^{\perp}]\cdot W(\vec{n}) .$$

Combining this with eqs.(2.6-8) finally gives

$$\mathrm{Tr}[\langle(T\nabla\vec{w})'\rangle_0] = \overline{\mathrm{Tr}}[T^S(\bar{\nabla}\bar{v} - v^{\perp}S)] + \overline{\mathrm{Tr}}[PWP(\bar{\nabla}\bar{v} - v^{\perp}S)]$$

$$+ [S(\bar{v}) + \mathrm{Grad}\, v^{\perp}]\cdot W(\vec{n}) + \mathrm{Tr}[\langle(T\nabla\vec{w}_n)'\rangle_0] \qquad (2.11)$$

as the surface source term for internal energy and -1 times that for the kinetic energy.

The other surface densities and current densities related to energy may be treated in similar fashion. We only quote the results. The convective kinetic energy current density is

$$P[\langle(\rho\frac{w^2}{2}\vec{w})'\rangle_0] = \tfrac{1}{2}\rho_0 V^2\bar{v} + \tfrac{1}{2}(\mathrm{Tr}W)\bar{v} + PW(\vec{V}) + \langle(\rho\frac{w_\ell^2}{2}\vec{w}_\ell)'\rangle_0 \qquad (2.12)$$

and the corresponding conductive current density is

$$-P[\langle(T(\vec{w}))'\rangle_0] = -T^S(\bar{v}) - P[W(\vec{V}) + \langle(T(\vec{w}_\ell))'\rangle_0] \,. \qquad (2.13)$$

Finally the internal energy convective current density is

$$P[\langle(u\vec{w})'\rangle_0] = u_0\bar{v} + P[\langle(u\vec{w}_\ell)'\rangle_0] \,. \qquad (2.14)$$

On comparing eqs.(2.3) and (2.11-14) with eqs. (II.4.3) and (II.4.9,10), we find that the general zeroth order theory embodies additional contributions, all of a similar nature, to the energy-related surface densities and current densities. It might be thought that the presence of these residual terms is a pathology peculiar to a Gibbs type of definition of the surface excess densities, and that some other kind of averaging would wipe them out. This is however most unlikely as their source is a nonlinearity that cannot be eluded. The consistency requirement (eq.(II.4.5)), which, to our knowledge, has hitherto been overlooked, already points to a difficulty even at the purely empirical level. This problem will require further investigation but, at the present time, we can only leave the matter as it stands.

REFERENCES

Addison,J.V.,and Schechter,R.S.[1978]. A.I.Ch.E.J. 24, 400.

Albano,A.M.,Bedeaux,D.,and Vlieger,J.[1979]. Physica 99A, 293.

Aris,R.[1962]. "Vectors,Tensors, and the Basic Equations of Fluid Mechanics". Prentice-Hall, Englewood Cliffs,N.J.

Aveyard,R.,and Vincent,B.[1977]. Prog. in Surface Sci. 8, 59.

Baret,J.F.[1968]. J. Chim. Phys. et Phys.-Chim. Biologique 65, 895.

Beaglehole,D.[1979]. Phys. Rev. Lett. 43, 2016.

Bedeaux,D.,Albano,A.M.,and Mazur,P.[1976]. Physica 82A, 438.

Bikerman,J.J.[1970]. "Physical Surfaces". Academic Press, New York and London.

Bikerman,J.J.[1973]. "Foams". Springer-Verlag, New York. Chap. 1.

Boruvka,L.,and Neumann,A.W.[1977]. J. Chem. Phys. 66, 5464.

Boussinesq,J.[1913]. Ann. Chim. Phys. 29, 349.

Brenner,H.,and Leal,L.G.[1978]. J. Colloid Interface Sci. 65, 191.

Brenner,H.[1979]. J. Colloid Interface Sci. 68, 422.

Buff,F.P.[1956]. J. Chem. Phys. 25, 146.

Buff,F.P.[1968]. In "Physics of Simple Liquids", John Wiley and Sons,Inc., New York.

Carey,B.S.,Scriven,L.E.,and Davis,H.T.[1978]. J. Chem. Phys. 69, 5040.

Courant,R.and Friedrichs,K.O.[1967]. "Supersonic Flow and Shock Waves". Interscience Publishers,Inc., New York.

Croxton,C.A.[1978]. "Progress in Liquid Physics". John Wiley and Sons, New York.

Deemer,A.R.,and Slattery,J.C.[1978]. Int. J. Multiphase Flow 4, 171.

Defay,R.,and Petré,G.[1971]. In "Surface and Colloid Science" (Ed. E. Matijevic), Vol. 3, Wiley, New York.

Defay,R.,Prigogine,I.,Bellemans,A.,and Everett,D.H.[1966]. "Surface Tension and Adsorption". Longmans,Green and Co.Ltd,London.

Defay,R.,Prigogine,I.,and Sanfeld,A.[1977]. J. Colloid Interface Sci. 58, 498.

De Groot,S.R.,and Mazur,P.[1969]. "Non-Equilibrium Thermodynamics". North-Holland Publishing Company, Amsterdam - London.

Ericksen,J.L.[1952]. J. Rat. Mech. Anal. 1, 521.

Georgescu,L.[1969]. Surface Sci. 15, 177.

Ghez,R.[1966]. Surface Sci. 4, 125.

Ghez,R.[1970]. Surface Sci. 20, 326.

Gibbs,J.W.[1961]. "The Scientific Papers",Vol. 1.Dover, New York.

Goodisman,J.[1979]. Phys. Rev. A 19, 1717.

Goodrich,F.C.[1973]. In "Progress in Surface and Membrane Science", Vol. 7.(Eds. J.F. Danielli,M.D. Rosenberg,and D.A. Cadenhead) Academic Press, New York.

Gray,P.[1968]. In "Physics of Simple Fluids".(Eds.H.N.V. Temperly, J.S. Rowlinson and G.S. Rushbrooke) John Wiley and Sons, Inc., New York.

Green,H.S.[1969]. "The Molecular Theory of Fluids". Dover, New York.

Guggenheim,E.A.[1965]. "Thermodynamique". Dunod, Paris.

Hennenberg,M.,Bisch,P.M.,Vignes-Alder,M.,and Sanfeld,A.[1980]. J. Colloid Interface Sci. 74, 495.

Hicks,N.J.[1965]. "Notes on Differential Geometry". Van Nostrand Reinhold Co. , New York.

Joly,M.[1964]. In "Recent Progress in Surface Science",Vol. 1.(Eds. J.F. Danielli,K.G.A. Pankhurst,and A.C. Riddiford) Academic Press, New York.

Kehlen,H.,and Baranowski,B.[1977]. J. Non-Equilib. Thermodyn. 2, 169.

Kirkwood,J.C.,and Buff,F.P.[1949]. J. Chem. Phys. 17, 338.

Kirkwood,J.G.,and Oppenheim,I.[1961]. "Chemical Thermodynamics". McGraw-Hill, New York.

Kitchener,J.A.[1964]. "Recent Progress in Surface Science".(Eds. J.F. Danielli,K.G.A. Pankhurst,and A.C. Riddiford) Academic Press, New York. Vol. 1,p. 57.

Kovac,J.[1977]. Physica 86A, 1;

Kreuzer,H.J.,and Beamish,J.[1977]. "Topics in Non-Equilibrium Physics". University of Alberta.

Krotov,V.V.,and Rusanov,A.I.[1972]. Colloid Journal 34, 255.

Landau,L.D.,and Lifshitz,E.M.[1966]. "Fluid Mechanics". Addison-Wesly Publishing Co.,Inc., Toronto.

Lekner,J.,and Henderson,J.R.[1978]. Physica 94A, 545.

Levich,V.G.,and Krylov,V.S.[1969]. Ann. Rev. Fluid Dyn. 1, 293.

Lucassen-Reynders,E.H.,and Lucassen,J.[1969]. Advan. Colloid Interface Sci. 2, 347.

Lucassen-Reynders,E.H.[1976]. In "Progress in Surface and Membrane Science",Vol. 10.(Eds. J.F. Danielli and D.A. Cadenhead) Academic Press, New York.

Melrose,J.C.[1968]. Ind. Eng. Chem. 60, 53.

Melrose,J.C.[1970]. Pure Appl. Chem. 22, 273.

Moeckel,G.P.,[1975]. Arch. Rat. Mech. Analysis 57, 255.

Murdoch,A.I.[1976]. Q. Jl Mech. Appl. Math. XXIX Pt.3, 245.

Mysels,K.J.,Shinoda,K.,and Frankel,S.[1959]. "Soap Films". Pergamon Press, New York.

Navascues,G.[1979]. Rep. Prog. Phys. (G.B.) 42, 1131.

Oh,S.G.,and Slattery,J.C.[1978]. J. Colloid Interface Sci. 67, 517.

Oldroyd,J.C.[1955]. Proc. Roy. Soc. Ser.A 232, 567.

O'Neil,B.[1970]. "Elementary Differential Geometry". Academic Press, New York and London.

Ostrach,S.[1979]. In "Physicochemical Hydrodynamics".(Ed.B.D. Spalding) Adv. Publ.Ltd, London.

Petrov,J.G.,and Miller,R.[1977]. Colloid and Polymer Sci. 255, 669.

Popielawski,J.[1970]. Surface Sci. 19, 355.

Prager,W.[1973]. "Introduction to Mechanics of Continua". Dover Publications Inc., New York. Chap. 3.

Reed,M.,and Simon,B.[1972]. "Methods of Modern Mathematical Physics". Academic Press, New York and London. Vol.1.

Ronis,D.,Bedeaux,D.,and Oppenheim,I.[1978]. Physica 90A, 487.

Samohýl,I.[1969]. Collection Czechoslov. Chem. Commun. 34, 2483.

Schwartz,L.[1959]. "Etude des sommes d'Exponentielles". Hermann Paris. P. 23.

Scriven,L.E.[1960]. Chem. Eng. Sci. 12, 98.

Scriven,L.E.,and Sternling,C.V.[1960]. Nature 16, 186.

Slattery,J.C.[1964]. Chem. Eng. Sci. 19, 379.

Slattery,J.C.[1967]. Ind. Eng. Chem. Fund. 6, 108.

Sternling,C.V.,and Scriven,L.E.[1959]. A. I. Ch. E. J. 5, 514.

Truesdell,C.,and Toupin,R.A.[1960]. "Handbuch der Physik".(Ed. S. Flügge) Springer-Verlag,Berlin. Vol.3/1, Sect.177.

Van den Tempel,M.,Lucassen,J.,and Lucassen-Reynders,E.H.[1965]. J. Phys. Chem. 69, 1798.

Vodák[1978 a]. Czech. J. Phys. B28, 833.

Vodák[1978 b]. Physica 93A, 244.

Waldmann,L.[1967]. Z. Naturforschung 22a, 1269.

Ward,A.F.H.,and Todai,L.[1946]. J. Chem. Phys. 14, 453.

Wolff,P.A.,and Albano,A.M.[1979]. Physica 98A, 491.